ABSTRACT

Treavor H. Boyer: Bench-Scale Testing of a Magnetic Ion Exchange Resin for Removal of Natural Organic Material
(Under the direction of Dr. Philip C. Singer)

The objective of this research was to compare enhanced coagulation with anion exchange for removal of disinfection by-product (DBP) precursors (i.e. natural organic matter (NOM) and bromide). Several anion exchange resins were evaluated for their capacity and rate of NOM and bromide removal. Treatment with a magnetic ion exchange resin (MIEX) was the primary focus of this study. Raw waters from four utilities in California were evaluated. The waters had low turbidity, low to moderate organic carbon concentrations, a wide range of alkalinities, and moderate to high bromide ion concentrations. Large volumes of treated water were generated using the appropriate doses of alum and MIEX as determined by preliminary jar-tests. The treated waters were compared based on removal of ultraviolet (UV) absorbance, dissolved organic carbon (DOC), trihalomethane formation potential (THMFP), and haloacetic acid formation potential (HAAFP). All four bromine- and chlorine-containing THMs (THM4) and all nine bromine- and chlorine-containing HAAs (HAA9) were analyzed. The waters were also fractionated before and after treatment to determine the molecular weight distribution and hydrophobic/hydrophilic character of the DOC. The results indicated that treatment with MIEX is more effective than coagulation at removing UV absorbance and DOC. Treatment with MIEX and treatment with MIEX followed by coagulation yielded similar results, suggesting that treatment with MIEX removes a wide fraction of organic matter including the fraction preferentially removed by coagulation. MIEX treatment reduced the THM4FP and HAA9FP in all waters, and did so to a greater extent than coagulation. Treatment with MIEX was most effective in raw waters having a high specific UV absorbance (SUVA) and a low anionic composition. Following MIEX treatment and subsequent chlorination, there was a shift to the more brominated THM and HAA species as compared to chlorination of the raw water. MIEX also removed bromide to varying degrees, depending on the raw water alkalinity and initial bromide ion concentration. Treatment with MIEX removed a greater amount and a wider range of organic acid fractions and molecular weight fractions than coagulation. Based on kinetic

studies, MIEX resin showed the fastest rate of removal of UV absorbance and DOC compared to three other traditional ion exchange resins that also exhibited a high capacity for removal of UV-absorbing materials and DOC.

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CHAPTER 1

INTRODUCTION

Chlorine is the most common oxidant and disinfectant used in drinking water treatment because it is an inexpensive and powerful oxidizing agent and disinfectant. Natural organic matter (NOM), a universal component of surface waters, is comprised of a variety of hydrophobic (humic) and hydrophilic compounds that arise from natural vegetative decay processes. When waters containing NOM and bromide are chlorinated, halogenated organic disinfection by-products (DBPs) are formed. These halogenated organic DBPs include trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, halopicrins, haloketones, cyanogen chloride, chloral hydrate, and halogenated furanones (Krasner et al. 1989, Singer 1994). THMs and HAAs are the two most common classes of halogenated organic DBPs and have been shown to account for approximately 50% of the total organic halide (TOX) concentration (Christman et al. 1983) in chlorinated drinking water.

In 1998 the U.S. Environmental Protection Agency (USEPA) finalized the Stage 1 Disinfectants/Disinfection By-Products Rule (D/DBPR) which lowered the maximum contaminant level (MCL) for THMs to 80 μg/L and established an MCL of 60 μg/L for HAAs (USEPA 1998). The Stage 1 D/DBPR was based on epidemiological studies that suggested an association between consumption of chlorinated drinking water and increased risk of certain types of cancer. Since the early 1990s, there have been individual human epidemiology studies which have found associations between acute exposure to high concentrations of DBPs by pregnant women and adverse reproductive or developmental effects such as spontaneous abortion and birth defects (Bove et al. 1995, Kanitz et al. 1996, Waller et al. 1998). In 2003 the USEPA proposed a new Stage 2 D/DBPR which maintains the same MCLs for THMs and HAAs but calculates compliance based on a locational running annual average (LRAA) instead of a system-wide running annual average (RAA) (USEPA 2003). The objective of the Stage 2 D/DBPR is to ensure that the RAA concentrations of THMs and HAAs are below their respective MCLs at all locations in the distribution system.

The source and chemical characteristics of NOM, along with other water quality parameters and chlorination conditions, have important implications for the concentration and speciation of the DBPs formed. To minimize DBP production, many water utilities have switched or are switching to alternative disinfectants, such as chloramines. Another option for water utilities is to remove DBP precursors (i.e. NOM and bromide) prior to disinfection, and to continue using free chlorine for robust disinfection. As regulations for DBPs become more stringent, improved DBP precursor removal strategies will be needed. Enhanced coagulation, a traditional precursor removal strategy, and anion exchange, a more novel precursor removal strategy, are two areas of active research for controlling DBP formation, as are nanofiltration membrane processes and activated carbon adsorption processes. Anion exchange is an especially exciting process because it has the potential to remove a larger fraction of NOM than coagulation and also may remove bromide (Singer and Bilyk 2002).

The concept of enhanced coagulation is to remove additional amounts of organic carbon beyond that traditionally removed when coagulation is applied for turbidity removal. Babcock and Singer (1979) demonstrated that coagulation preferentially removes DBP precursors compared to overall removal of total organic carbon (TOC). Utilities with raw waters having low TOC concentrations and high alkalinities tend to have the most difficulty in removing DBP precursors by coagulation (White et al. 1997). A disadvantage of enhanced coagulation is that it removes hydrophobic organic carbon to a much greater extent than the hydrophilic fraction (Babcock and Singer 1979, Owen et al. 1995, Liang and Singer 2003). As a result, enhanced coagulation is often an ineffective DBP control strategy for waters with a substantial fraction of hydrophilic NOM.

A magnetic ion exchange resin (MIEX), developed by Orica Watercare of Victoria, Australia, was designed specifically to remove dissolved organic carbon (DOC) from raw drinking water. A novel property of the MIEX resin is the impregnation of magnetized iron oxide into the polymer matrix. The magnetic component aids settling of the resin and allows the resin beads to be smaller so that they can be applied to raw water in a slurry form. Instead of being used in a fixed-bed like traditional ion exchange resins, MIEX is designed to be suspended in a completely mixed flow reactor. Because MIEX is

smaller than traditional ion exchange resins and because it is suspended in the reactor, MIEX removes NOM much faster than traditional ion exchange resins (Slunjski et al. 2002).

Bench-scale testing of MIEX using doses of 5-10 mL/L has illustrated rapid rates of NOM removal, with the majority of ultraviolet (UV)-absorbing organics removed in the first 10-20 minutes (Singer and Bilyk 2002, Lee et al. 2003, Johnson and Singer 2003). An additional benefit of treatment with MIEX is that it has been shown to remove bromide (Singer and Bilyk 2002, Johnson and Singer 2003). MIEX has been shown to remove both hydrophobic and hydrophilic organic carbon, and organic materials with a wide range of molecular weights (Singer and Bilyk 2002, Lee et al. 2003).

The objective of this research was to compare enhanced coagulation with anion exchange for removal of DBP precursors. Raw waters with various levels of TOC, turbidity, alkalinity, and bromide from four different water utilities in California were chosen for this project, which was conducted as part of a larger study sponsored by Cal-Fed. Several anion exchange resins were evaluated for their capacity to remove NOM and bromide and for the rate at which they remove these DBP precursors. Treatment with MIEX was the primary focus of this study. The impacts of enhanced coagulation and treatment with MIEX were analyzed based on removal of UV absorbance, DOC, THM formation potential (THMFP), and HAA formation potential (HAAFP). The DOC in the raw waters and treated waters was fractionated to evaluate the relationship between treatment and NOM characteristics.

CHAPTER 2

LITERATURE REVIEW

2.1 NATURAL ORGANIC MATTER

NOM is a general term used to describe a complex mixture of aromatic and aliphatic organic macromolecules resulting from the breakdown of aquatic and terrestrial flora. Allochthonous organic matter enters a water body from the terrestrial watershed whereas autochthonous organic matter is derived from biota growing in the water body (Croue et al. 1999). Whether NOM is derived from soil or the aquatic environment has an effect on its physical and chemical characteristics, such as polarity, solubility, hydrophilicity, molecular weight, and elemental composition. NOM is often referred to as refractory because the rates of biodegradation are slow compared to other organic matter.

NOM is ubiquitous in surface waters. Its concentration can range from less than 1 mg/L to greater than 50 mg/L in bogs and swamps (Letterman et al. 1999). Drinking water treatment practices are strongly influenced by the concentration and nature of NOM. NOM can cause aesthetic problems by imparting taste, odor, and color to water (Leenheer and Croue 2003). Coagulation literature and practice suggest that the amount and character of the NOM influences the coagulant dose (Dempsey et al. 1984, Harrington 1997, Letterman et al. 1999). NOM is responsible for fouling membranes and ion exchange resins (Kunin 1972, Clifford 1999, Taylor and Wiesner 1999). NOM in the distribution system can lead to biofilms. NOM is the dominant precursor material for DBPs. Also of increasing interest are low concentration organic micropollutants, such as pesticides, which can partition into and sorb onto the NOM.

2.1.1 Chemistry

The chemistry of NOM can be described in terms of polarity or hydrophobicity, aromatic, unsaturated, and aliphatic carbon, functional group chemistry, elemental

composition, and molecular weight. The more hydrophobic or non-polar fractions of organic matter are commonly referred to as humic substances. Humic substances can be further divided into humic acids, fulvic acids, and neutrals. By definition, humic acids are those humic substances that precipitate at pH 1, while fulvic acids stay in solution at pH 1 (Stumm and Morgan 1996). Humic acids have a higher aromatic carbon content than fulvic acids, whereas fulvic acids are more aliphatic and have more carboxylic and phenolic groups (Owen et al. 1995, Krasner et al. 1996).

Non-humic organic matter is not well defined and is characterized as hydrophilic or polar. Spectra from ^{13}C-NMR showed that hydrophilic fractions are distinctly different from hydrophobic fractions (Wong et al. 2002). NMR spectra of the hydrophobic fractions exhibit the general features of aliphatic, alkoxyl, unsaturated, and carbonyl carbons, whereas the hydrophilic fractions are dominated by alkoxyl carbon attributed to carbohydrates. In general the aromatic content of humic acids is greater than fulvic acids which are greater than hydrophilic organic matter (Reckhow et al. 1990, Krasner et al. 1996). Fulvic acids and hydrophilic organic matter have a greater concentration of carboxylic acid functional groups than humic acids (Owen et al. 1995). As a result, fulvic acids and hydrophilic organic matter have a higher charge density and are therefore more difficult to chemically coagulate by charge neutralization.

The molecular weight distribution of NOM can range from less than 500 Daltons to greater than 30,000 Daltons (Collins et al. 1986, Pelekani et al. 1999, Leenheer and Croue 2003). A significant fraction of aquatic NOM is believed to have molecular weights in the <1,000-10,000 Dalton range. In polymer chemistry, polydispersivity is defined as the ratio of weight-average molecular weight to number-average molecular weight and reflects the breadth of the molecular weight distribution (Painter and Coleman 1997). Using high performance size exclusion chromatography, Chin et al. (1994) showed that humic substances are smaller and less polydisperse than previously believed. There have also been attempts to relate chemical structure to molecular weight, such as the work by Collins et al. (1986) which showed that the carboxyl content of humic substances appears to be inversely related to molecular weight. Often, treatment processes such as coagulation are not effective at removing the lower molecular weight fractions (Collins et al. 1986, Owen et al. 1995). Other researchers have shown that the

low molecular weight fractions produce more THMs than the bulk NOM when normalized for chlorine demand (Kim and Symons 1991, Owen et al. 1995).

2.1.2 Characterization

NOM can be dissolved, particulate, and associated with colloids. NOM cannot be measured directly, but surrogate measurements such as UV absorbance, TOC, and DOC can provide insight into the nature and concentration of NOM. UV absorbance at 254 nm (UV254) gives an indication of the aromaticity of the NOM (Edzwald et al. 1985). TOC and DOC can help quantify the particulate and soluble organic carbon concentrations of NOM. DOC is operationally defined as the organic carbon concentration of a water filtered through a 0.45 μm filter. For most waters, DOC is greater than 90% of TOC (Harrington 1997). The specific UV absorbance (SUVA) is defined as the ratio of UV254 to DOC and is strongly correlated with aromatic content (Croue et al. 1999). In general, the SUVA for humic acids is greater than the SUVA for fulvic acids which is greater than the SUVA for the hydrophilic fraction (Edzwald et al. 1985, Reckhow et al. 1990, Croue et al. 1999).

Other techniques used to characterize NOM include resin fractionation, size exclusion chromatography (SEC), ultrafiltration (UF), DBP formation potential (FP), elemental analysis, and acidity titration. The Amberlite XAD-8/Amberlite XAD-4 resin fractionation technique is a standard method for characterizing NOM (Thurman and Malcolm 1981, Leenheer 1981, Aiken et al. 1992). The XAD-8/XAD-4 fractionation method isolates three organic acid fractions: hydrophobic acids (HPOA), transphilic acids (TPHA), and hydrophilic acids (HPIA). The HPOA fraction is retained on the XAD-8 resin, the TPHA fraction is retained on the XAD-4 resin, and the HPIA fraction passes through both columns. The TPHA fraction is characterized by intermediate polarity and is also known as XAD-4 acid or syn-fulvic acid. In most natural waters, the HPOA and TPHA fractions can account for 60-70% of the DOC (Croue et al. 1999).

Two common methods of characterizing the molecular weight distribution of NOM are SEC and UF. SEC can provide high-resolution molecular weight data whereas UF provides low-resolution apparent molecular weight (AMW) data. A typical SEC set-

up consists of a pump, a packed column, and a detector(s). SEC separates NOM based on hydrodynamic diameter, with larger molecular weight fractions eluted first and smaller molecular weight NOM eluted later. Detectors can include DOC, UV absorbance, and fluorescence. A great deal of research has focused on characterizing NOM using SEC (Chin et al. 1994, Pelekani et al, 1999, Specht and Frimmel 2000, Wong et al. 2002). Molecular weight fractionation by UF is achieved by passing water through membranes with nominal molecular weight cutoffs of 500-30,000 Daltons. The effluent is then analyzed for DOC and UV absorbance. UF cannot provide absolute molecular weights, but it is a useful technique for comparing molecular weight distributions. Collins et al. (1986) found comparable trends in molecular weight between UF and SEC.

Bulk and fractionated NOM can also be chlorinated and analyzed for THMs, HAAs, and TOX. Croue et al. (1999) found good correlation between SUVA and TOXFP, THMFP, and trichloroacetic acid (Cl_3AA) formation potential. Others have found that the humic acid fraction always yields more THMs than the fulvic acid fraction (Babcock and Singer 1979, Reckhow et al. 1990). Liang and Singer (2003) showed that when coagulated waters were chlorinated, the removal of HAAFP was always greater than the removal of THMFP. Since hydrophobic carbon has been shown to be preferentially removed by coagulation, these results suggest that hydrophilic carbon is an important THM precursor material.

Elemental analysis can be used to quantify the carbon (C), hydrogen (H), oxygen (O), nitrogen (N), and sulfur (S) content of NOM (Krasner et al. 1996, Croue et al. 1999, Schwarzenbach et al. 2003). The C to H ratio is commensurate with the degree of unsaturated carbon and/or aromatic carbon, that is, as the C to H ratio increases the amount of unsaturated and/or aromatic carbon increases. NOM can be titrated to determine its total acidity and carboxylic acidity. The phenolic hydroxyl acidity can then be determined by difference.

In summary, the humic fraction of NOM is characterized by the following: high SUVA (greater than 3 L $mg^{-1}m^{-1}$), hydrophobic, aromatic, larger molecular weight, preferentially removed by coagulation, and dominant precursor material for THMs and HAAs (Babcock and Singer 1979, Edzwald et al. 1985, Collins et al. 1986, Reckhow et al. 1990, Owen et al. 1995, Krasner et al. 1996, Croue et al. 1999, Wong et al. 2002,

Liang and Singer 2003). The non-humic fraction of NOM is characterized by: low SUVA (less than 3 L $mg^{-1}m^{-1}$), hydrophilic, aliphatic, and smaller molecular weight.

2.2 BROMIDE

Many coastal areas of the United States have drinking water sources that contain moderate to high concentrations of bromide. Both surface waters and groundwater can have elevated levels of bromide. Low to moderate bromide waters have concentrations in the 10-100 µg/L range. High bromide waters can have bromide concentrations in excess of 1 mg/L (Standard Methods 1998). Bromide is not harmful, but it does serve as a precursor for DBPs, such as bromate and halogenated bromine-containing organic compounds. Sources of bromide include salt water intrusion, connate water (ancient, geological water), oil-field brines, and industrial, municipal, and agricultural run-off. Many coastal areas experience seasonal variations in bromide concentrations due to saltwater intrusion. An example of the seasonal variation in bromide concentration is the San Francisco Bay Delta area which serves as a drinking water source for municipalities in northern and southern California. During the wet season, freshwater flows prevent saltwater from backing into the Delta, but during dry periods saltwater intrusion from the Bay can result in elevated bromide concentrations.

In raw drinking waters containing bromide, chlorine will oxidize the bromide to hypobromous acid (HOBr) (Singer and Reckhow 1999):

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (2\text{-}1)$$

This reaction is very fast. HOBr has a pK_a of 8.7 at 25°C and will dissociate to form the hypobromite ion (OBr^-), depending upon pH:

$$HOBr \leftrightarrow OBr^- + H^+ \quad (2\text{-}2)$$

HOBr can react with NOM to form brominated DBPs, such as bromoform ($CHBr_3$), and both HOBr and HOCl can react with NOM to form mixed chlorinated and brominated DBPs, such as bromodichloroacetic acid ($BrCl_2AA$). Under typical water treatment plant conditions, more hypobromous acid will be in the HOBr form than hypochlorous acid in the HOCl form. Since the undissociated acid is a stronger oxidant, there will be a greater tendency for bromine-substituted DBPs (Pourmoghaddas et al. 1993, Cowman and Singer

1996, Singer and Reckhow 1999). Bromine-substituted DBPs are of particular interest because they have been shown to be more toxic and/or carcinogenic than their chlorinated analogs (Kargalioglu et al. 2000, McDorman et al. 2003)

2.3 CHEMISTRY OF CHLORINE

Since chlorine was first introduced to disinfect water at Bubbly Creek, Chicago in 1908, it has remained a dominant choice for oxidation and disinfection for water treatment (Haas 1999). Chlorine has remained a popular disinfectant because hypochlorous acid is a powerful oxidant and disinfectant and chlorine has a lasting residual in distribution systems. A common form of chlorine used for disinfection and oxidation in water treatment is sodium hypochlorite (NaOCl). In water, sodium hypochlorite completely dissociates to the hypochlorite ion (Haas 1999):

$$NaOCl \rightarrow Na^{+} + OCl^{-} \qquad (2\text{-}3)$$

The concentration of hypochlorite ion and hypochlorous acid are dependent upon pH ($pK_a = 7.5$ at 25°C):

$$HOCl \leftrightarrow OCl^{-} + H^{+} \qquad (2\text{-}4)$$

Hypochlorous acid is a stronger oxidizing agent and disinfecting agent than hypochlorite ion, so the most effective oxidation and disinfection takes place at pH < 7.5. Reactions involving chlorine can be a combination of oxidation, substitution, and addition reactions (Singer and Reckhow 1999). Common compounds encountered in water treatment which exert a chlorine demand include ammonia, organics, bromide, sulfide, and reduced metals (Singer and Reckhow 1999, Haas 1999). Free chlorine can react with the ammonium ion to form chloramines. Chlorine can oxidize amino acids to non-halogenated compounds, such as aldehydes and organic acids. Chlorine can oxidize bromide to hypobromous acid, as detailed above. Free chlorine can also be used to oxidize reduced iron and manganese to form insoluble metal precipitates prior to solid-liquid separation. Through a combination of oxidation, addition, and substitution reactions, chlorine can react with NOM to form halogenated organics like THMs and HAAs.

2.4 DISINFECTION BY-PRODUCTS

2.4.1 Background

The term DBP is a generic term used to describe the product(s) of any reaction between a disinfectant or oxidant and precursor material. There are three common classes of DBPs: oxidation, inorganic, and halogenated organic DBPs. Oxidation by-products are formed, for example, from the ozonation of NOM (e.g. aldehydes and aldo and ketoacids) (Singer and Reckhow 1999). Bromate (BrO_3^-), a by-product of the ozonation of bromide-containing waters, and chlorite (ClO_2^-), a decay product of chlorine dioxide disinfection, are two regulated inorganic DBPs (USEPA 1998). Halogenated organic DBPs are formed by the chlorination of water containing NOM and bromide. Halogenated organic DBPs include THMs, HAAs, haloacetonitriles, halopicrins, haloketones, cyanogen chloride, chloral hydrate, and halogenated furanones. The two most common groups of halogenated organic DBPs are THMs and HAAs (Christman et al. 1983, Krasner et al. 1989). Table 2.1 shows the four bromine- and chlorine-containing THMs (THM4), and the nine bromine- and chlorine-containing HAAs (HAA9).

Table 2.1 Trihalomethane and Haloacetic acid species

Trihalomethanes	THM4
Chloroform	Cl_3CH
Bromodichloromethane	$BrCl_2CH$
Dibromochloromethane	Br_2ClCH
Bromoform	Br_3CH
Haloacetic Acids	HAA9
Chloroacetic Acid	ClAA
Bromoacetic Acid	BrAA
Dichloroacetic Acid	Cl_2AA
Bromochloroacetic Acid	BrClAA
Dibromoacetic Acid	Br_2AA
Trichloroacetic Acid	Cl_3AA
Bromodichloroacetic Acid	$BrCl_2AA$
Dibromochloroacetic Acid	Br_2ClAA
Tribromoacetic Acid	Br_3AA

During the 1980s, as DBPs continued to attract attention in the drinking water treatment arena, an attempt was made to survey DBPs in U.S. drinking waters. A study by Krasner et al. (1989) surveyed 35 water utilities nationwide. Important observations from the study were that THMs constituted the largest fraction of measured DBPs, with THMs being dominated by chloroform, and HAAs constituted the second largest fraction of measured DBPs, with HAAs being dominated by trichloroacetic acid and dichloroacetic acid. Only five of the nine HAAs (HAA5) from Table 2.1 were measured by Krasner et al. (1989) (e.g. ClAA, Cl_2AA, Cl_3AA, BrAA, and Br_2AA). The study reported a median THM4 concentration of 39 µg/L and a median HAA5 concentration of 19 µg/L (Krasner et al. 1989). It should be noted that in waters containing high bromide concentrations, tribromoacetic acid, dibromochloroacetic acid, bromodichloroacetic acid, and bromochloroacetic acid can have appreciable concentrations at the expense of dichloroacetic acid and trichloroacetic acid (Pourmoghaddas et al. 1993, Cowman and Singer 1996, McLain et al. 2002, Obolensky and Singer 2003). Therefore, for waters with a high concentration of bromide, HAA5 under-represents the true concentration of HAAs. An observation which would impact regulatory thinking was that since there appeared to be a strong correlation between THM4 and the sum of all measured DBPs, if a utility were able to control its THM levels, it should reflect control of other known and unknown halogenated organic DBPs.

Singer et al. (1995) evaluated DBP levels in chlorinated North Carolina drinking water to compare observations with the earlier study by Krasner et al. (1989). Six North Carolina utilities were tested. The raw water characteristics for all of the utilities were similar, with moderate to high concentrations of TOC, high humic content, low alkalinity, and low bromide concentrations. They observed that both THM4 and HAA5 accounted for about 15% of the TOX concentration. Since chloroform was observed to be the dominant THM species, it was expected that trichloroacetic acid and dichloroacetic acid would be the dominant HAA species, and in fact, this is what was observed. Singer et al. (1995) suggested that the concentration of HAAs in finished drinking water may be much higher than indicated by the Krasner et al (1989) study, especially for utilities that chlorinate their water at an acidic pH or have elevated levels of bromide in their source water or both.

2.4.2 Precursors and Chemistry

Important factors affecting halogenated organic DBP formation are: nature and concentration of NOM, pH of chlorination, chlorination contact time, temperature, and bromide concentration. Rook (1974, 1976) proposed that chlorine reacted with humic substances in natural waters to produce chloroform and other haloforms. Others verified that when humic acids were chlorinated, chloroform and other trihalogenated organic compounds were formed (Bellar et al. 1974, Stevens et al. 1976, Babcock and Singer 1979). Research by Christman et al. (1983) attempted to identify and quantify major halogenated products of fulvic acid chlorination. They found that chlorination of fulvic acid isolated from natural surface water yielded four principal products: chloroform, trichloroacetic acid, dichloroacetic acid, and dichlorosuccinic acid which accounted for approximately 53% of the measured TOX concentration. They also identified over 100 other DBP species (Christman et al. 1983).

Because it had been observed that the humic fraction of NOM was the dominant precursor material for most DBPs, researchers sought to determine whether the humic acids or the fulvic acids were more important precursors. Babcock and Singer (1979) found that chloroform formation and chlorine consumption increased as the concentration of humic acid increased, and that chlorination of fulvic acid produced chloroform, but in smaller amounts than produced by the humic acid fraction. Later work by Reckhow et al. (1990) showed that when humic materials were chlorinated, the humic acid fraction produced higher concentrations of chloroform, trichloroacetic acid, dichloroacetic acid, and dichloroacetonitrile than the corresponding fulvic acid fraction, but the fulvic acid fraction produced higher concentrations of 1,1,1-trichloroacetone. Recently, Gallard and von Gunten (2002) examined the kinetics of chlorination and of THM formation. They observed that resorcinol-type moieties can only explain the rapid initial formation of THMs from natural waters and that phenol-type moieties seemed consistent with the kinetics of slow THM formation.

The pH of chlorination affects the ratio of THMs to HAAs and the distribution of HAA species. It was observed by Stevens et al. (1976) that the humic substances forming THMs were more reactive at higher pH. It has been shown by several

researchers (Reckhow et al. 1990, Pourmoghaddas et al. 1993, Liang and Singer 2003) that the concentration of THM4 increases with increasing pH whereas the concentration of HAA9 decreases with increasing pH. In particular, the concentrations of dihaloacetic acids (X_2AAs) is relatively constant with changing pH of chlorination, but the concentrations of trihaloacetic acids (X_3AAs) decreases with increasing pH. In a survey of halogenated organic DBPs at six North Carolina utilities, Singer et al. (1995) observed that the mean and median trichloroacetic acid and dichloroacetic acid concentrations were almost as high as the corresponding chloroform concentrations. They concluded this was probably attributable to the slightly acidic pH values for chlorination.

Both THM and HAA concentrations increase with increasing chlorine contact time. Higher chlorine doses and chlorine residuals favor HAA formation over THM formation, X_3AA formation over X_2AA formation and monohaloacetic acid (XAA) formation, and formation of chlorinated DBPs over brominated DBPs (Liang and Singer 2003). Seasonal variations in the concentration of THMs and HAAs (e.g. high concentrations of DBPs in the summer and low concentrations in the winter) are usually attributable to temperature. Both THM and HAA concentrations increase with increasing temperature (Stevens et al. 1976).

When waters containing bromide are chlorinated, mixed halogenated and fully brominated DBPs can be formed. As the ratios of bromide to TOC (Br/TOC) and bromide to chlorine (Br/Cl_2) increase, the speciation of THMs and HAAs shifts toward the more brominated species (Liang and Singer 2003). Pourmoghaddas et al. (1993) concluded, based on experimental observations and the literature, that the bromine atom is more reactive than the chlorine atom during the halogenation of THM precursors. This conclusion was corroborated by McLain et al. (2002) when they noted that greater concentrations of bromine-substituted DBPs were formed when organic matter limited the reaction, reflecting the faster kinetics of bromine incorporation.

It has been observed that the average percentage of bromine-substituted THMs increased as influent bromide concentrations increased (McLain et al. 2002). Pourmoghaddas et al. (1993) observed that the concentrations of dichloroacetic acid and trichloroacetic acid both decreased as the concentration of bromide increased, indicating a shift to the more brominated species. Cowman and Singer (1996) verified that, for low

bromide waters (< 3 μM), dichloroacetic acid and trichloroacetic acid were the dominant HAA species, but as bromide concentrations increased to > 20 μM, tribromoacetic acid and dibromoacetic acid became the dominant HAA species. From an analysis of the Information Collection Rule (ICR) database, at the highest bromide concentrations, bromochloroacetic acid and dibromoacetic acid were the dominant HAA species (McLain et al. 2002, Obolensky and Singer 2003). Bromodichloroacetic acid and dibromochloroacetic acid can also be significant for waters with high bromide ion concentrations (McLain et al. 2002).

A normalized bromine incorporation factor (Br_XDBP) can be defined for THM4, X_2AA, and X_3AA to quantitatively analyze bromine substitution with respect to overall halogen substitution. The Br_XDBP is defined as the ratio of molar bromine to molar halogen according to the following equations:

$$Br\_THM4 = \frac{0 \cdot Cl_3CH + 1 \cdot BrCl_2CH + 2 \cdot Br_2ClCH + 3 \cdot Br_3CH}{3 \cdot (Cl_3CH + BrCl_2CH + Br_2ClCH + Br_3CH)} \quad (2\text{-}5)$$

$$Br\_X_2AA = \frac{0 \cdot Cl_2AA + 1 \cdot BrClAA + 2 \cdot Br_2AA}{2 \cdot (Cl_2AA + BrClAA + Br_2AA)} \quad (2\text{-}6)$$

$$Br\_X_3AA = \frac{0 \cdot Cl_3AA + 1 \cdot BrCl_2AA + 2 \cdot Br_2ClAA + 3 \cdot Br_3AA}{3 \cdot (Cl_3AA + BrCl_2AA + Br_2ClAA + Br_3AA)} \quad (2\text{-}7)$$

Using the ICR database, Obolensky and Singer (2003) showed that the extent of bromine substitution in X_2AAs closely mirrored that in THM4, while the extent of bromine substitution in X_3AAs was approximately 20% lower than in THM4. An interesting observation by Cowman and Singer (1996) was that the mole fraction of X_3AA (61-67%), X_2AA (30-36%), and XAA (3-5%) appeared to be independent of bromide concentration.

It has been observed that the hydrophilic fraction of NOM is more reactive with bromine than the corresponding hydrophobic fraction, and that bromine-containing species comprised a higher molar proportion of THMs than HAAs (Liang and Singer

2003). This seems plausible since the hydrophilic fraction is believed to be more important precursor material for THMs than for HAAs.

2.4.3 Regulations

In 1979 the USEPA promulgated the first DBP Rule establishing an MCL of 100 μg/L for THM4 for utilities serving greater than 10,000 people (USEPA 1979). The regulation was based on an RAA of four quarterly samples taken systemwide. This rule was based on epidemiological studies that showed a slightly increased risk of bladder, colon, and rectal cancer from long-term exposure to chlorinated drinking water. This was an interim rule and was to be re-evaluated after more data on DBPs and health effects were collected. The National Cancer Institute (Cantor et al. 1987, 1998) conducted several epidemiological studies suggesting a link between chlorinated drinking water and cancer and adverse reproductive and developmental health effects. In 1992 the USEPA initiated a negotiated rule-making (RegNeg) approach for regulating DBPs in drinking water (Means and Krasner 1993, Singer 1994). The RegNeg process brought together the USEPA and other interested parties, such as the American Water Works Association and drinking water experts from academia, consulting firms, and water utilities, as well as citizen advocacy groups. A result of the RegNeg process was promulgation of the ICR in 1996 and a framework for the Stage 1 and Stage 2 D/DBPRs. The ICR was established to compile a database of DBP species and concentrations to aid in drafting more comprehensive DBP regulations. The ICR data were collected over an 18-month period from 1997-98 from water utilities serving greater than 100,000 people (USEPA 1996).

In November, 1998 the USEPA finalized the Stage 1 D/DBPR which applies to all community water supplies. The Stage 1 D/DBPR lowered the MCL for THM4 to 80 μg/L and established an MCL of 60 μg/L for five of the nine HAAs (HAA5). HAA5 included ClAA, Cl_2AA, Cl_3AA, BrAA, and Br_2AA. These five HAA species were chosen for regulation based on occurrence data and because there was no standard method at the time for analyzing the other HAA species. Like the original 1979 THM Rule, these MCLs were based on an RAA of four quarterly samples taken systemwide (USEPA 1998). The USEPA defined the best available technology for complying with

the Stage 1 D/DBPR to be enhanced coagulation for removal of TOC. Table 2.2 is the TOC-alkalinity matrix which outlines the percent TOC removal required using enhanced coagulation as defined in the Stage 1 D/DBPR (USEPA 1998). The Stage 1 D/DBPR was designed to minimize risk from long-term exposure to halogenated organics in drinking water.

Table 2.2 Percent TOC removals required for enhanced coagulation

Source Water TOC (mg/L)	Source Water Alkalinity (mg/L as $CaCO_3$)		
	< 60	60-120	> 120
< 2.0	No Action	No Action	No Action
2.0-4.0	35%	25%	15%
4.0-8.0	45%	35%	25%
> 8.0	50%	40%	30%

Since the early 1990s, there have been several epidemiology studies which have found associations between acute exposure to high concentrations of DBPs by pregnant women and adverse reproductive or developmental effects such as spontaneous abortion and birth defects (Bove et al. 1995, Kanitz et al. 1996, Waller et al. 1998). Recent epidemiological studies do not provide any conclusive evidence either for or against the association between short-term exposure to high concentrations of DBPs by pregnant women and adverse reproductive or developmental effects (Shaw et al. 2003, Waller et al. 2003, Zender et al. 2003). Due to the possibility of adverse health effects from short-term exposure to high concentrations of DBPs in chlorinated drinking water, in August, 2003 the USEPA proposed the Stage 2 D/DBPR for all community water supplies. A final Stage 2 D/DBPR is expected in 2005.

The objective of the Stage 2 D/DBPR is to provide equity with respect to DBP protection, regardless of location in the distribution system. The MCLs for THM4 and HAA5 will remain unchanged, but instead of calculating concentrations based on a systemwide RAA, an LRAA will be implemented. The locations for calculating the LRAA will be sites in the distribution system that represent the highest THM4 and HAA5 levels. By ensuring that all locations within the distribution system meet the 80 µg/L THM4 and 60 µg/L HAA5 MCLs, it is expected that risk due to short-term exposure to high concentrations of DBPs will be minimized (USEPA 2003).

2.4.4 Control and Removal Strategies

Early recommendations for controlling THMs and HAAs were to move the point of chlorination to a location after settling or filtration (Stevens et al. 1976, Babcock and Singer 1979). Other strategies for controlling DBPs included switching to an alternative disinfectant, removing the DBPs after they have formed, and removing the precursor material. A common approach for DBP control practiced by many utilities was to switch to chloramination for secondary disinfection. Research has shown that DBP production is minimized by chloramination (Cowman and Singer 1996), but more recent research has revealed potential deleterious aspects of chloramination, such as the possibility of nitrification problems in the distribution system and the production of NDMA (Wilczak et al. 2002). Removing DBPs once they have formed in the treatment plant is typically not a viable option. The USEPA cites the best available technology for controlling THMs and HAAs as enhanced coagulation which is a technique for precursor removal. Other methods of precursor removal include membrane filtration, granular activated carbon (GAC) adsorption, and anion exchange.

Since most treatment processes for precursor removal focus on removing TOC, the Br/TOC ratio increases. In Section 2.4.2, it was noted that as the Br/TOC ratio is increased, there is a shift to the more brominated THMs and HAAs. This can be a concern because mixed and fully brominated DBPs have been shown to pose a greater health risk than their chlorinated analogs (Kargalioglu et al. 2000). Summers et al. (1993) evaluated GAC, powdered activated carbon, anion exchange, and membrane filtration for removal of DOC and found that all of these processes were most effective at controlling chloroform formation and least effective at controlling bromoform production. Black et al. (1996) suggested that if the more brominated DBPs have a greater cancer risk, then it is possible that reducing TOC concentrations could actually increase the cancer risk. Enhanced coagulation and anion exchange for precursor removal will be detailed below since these were the treatment processes investigated in this study.

2.4.4.1 Enhanced Coagulation

The objective of enhanced coagulation is to remove additional amounts of organic carbon beyond that traditionally removed when coagulation is applied for turbidity removal. Kavanaugh (1978) demonstrated that modified coagulation can remove a substantial but unidentified fraction of organic material found in natural waters. Other researchers investigated the mechanisms of coagulation of humic substances by aluminum salts to better understand coagulation of NOM (Dempsey et al. 1984). Under the Stage 1 D/DBPR, utilities are required to remove a specific amount of TOC based on their raw water TOC concentration and alkalinity (see Table 2.2 § 2.4.3). If a utility cannot meet this requirement, they must demonstrate, through jar-testing, a coagulant dose corresponding to the point of diminishing returns (PODR). The PODR is determined to occur when 10 mg/L of additional alum does not decrease residual TOC concentration by at least 0.3 mg/L (Krasner and Amy 1995). Jar-test evaluations have found that a significant fraction of utilities will not meet the TOC removal requirements (Krasner and Amy 1995, White et al. 1997). Utilities with raw waters having low concentrations of TOC and high alkalinities will have the most difficulty in meeting TOC removal requirements. Coagulation has been shown to preferentially remove the high molecular weight, hydrophobic organic carbon fraction of NOM (Harrington 1997, White et al. 1997). As a result, coagulated water has a lower SUVA than the corresponding raw water. Since coagulation preferentially removes UV-absorbing, hydrophobic organic matter, large reductions in HAAFP and THMFP are expected, with greater reductions in the HAAFP compared to the THMFP (Liang and Singer 2003).

2.4.4.2 Ion Exchange

There are three common ion exchange theories: crystal lattice exchange theory, double-layer theory, and Donnan membrane theory (Kunin 1972). Double-layer theory is useful in explaining the coagulation of particles and colloids with metal salts. Crystal lattice exchange theory and Donnan membrane theory provide a theoretical framework for explaining the exchange phenomena in ion exchange resins. Ion exchange resins are

composed of a porous polymer matrix which has covalently bound positive or negative functional groups. Associated with these fixed functional groups, through electrostatic forces, are mobile counter-ions. In the case of anion exchange resins, the covalently bound functional groups are positively charged and the associated mobile counter-ions have a negative charge. The thermodynamics of ion exchange are governed by the activity of the mobile counter-ions with respect to the activity of anionic species in bulk solution. This difference in activities translates to a chemical potential driving force, resulting in the exchange of counter-ions on the resin for anionic species in bulk solution. Even if the thermodynamics of ion exchange are favorable, ion exchange resins do not have the same selectivity for all ionic species. The exchange potential of an anionic species in bulk solution and a counter-ion in the resin phase will depend on the relative charges and ionic radii of the two ions. In general, the greater the charge and the smaller the ionic radius the greater is the exchange potential (Kunin 1972). For a typical strong-base anion exchange resin, Kunin and Myers (1949) found the order of decreasing exchange potential to be: sulfate > chromate > citrate > tartrate > nitrate > arsenate > phosphate > molybdate > acetate = iodide = bromide > chloride > fluoride > hydroxide. Since ion exchange resins have a finite number of exchange sites, the resins become exhausted and must be regenerated. Depending on the nature of an anion exchange resin, it can be regenerated with hydrochloric acid, sodium hydroxide, or sodium chloride. The mechanism of regeneration is analogous to the ion exchange mechanism described above, in that chemical potential serves as the driving force for contaminant removal and replacement with the original counter-ion. This is done with a high concentration of the regenerating solution in order to reverse the conventional exchange process.

Ion exchange has traditionally been used in water treatment for softening hard water via cation exchange. These cation exchange resins exchange sodium on the resin for calcium and magnesium in solution. An area of growing research is the use of anion exchange resins for removal of NOM (Singer and Bilyk 2002, Bolto et al. 2002a, 2002b, Lee et al. 2003). Most natural waters have a pH between 6 and 9 (Stumm and Morgan 1996). Under these conditions, carboxylic acid functional groups of the NOM are deprotonated, resulting in a net negative charge on the NOM. If the ion exchange resin has a greater affinity for the NOM than for the counter-ion, the NOM will be exchanged

and removed from solution. Fu and Symons (1990) were the first to conduct a comprehensive study to quantify the mechanism of anion exchange, and concluded that ion exchange (not sorption) was the dominant removal mechanism for all molecular weight fractions of NOM.

Anion exchange resins can be classified based on polymer composition, porosity, and basicity. The structural matrix of most anion exchange resins is a copolymer of styrene or acrylate with divinylbenzene. Styrene-type resins are more hydrophobic and sorb less water than acrylate-type resins. Therefore, acrylate-type resins tend to have a more open structure and a higher water content (Fu and Symons 1990, Clifford et al. 1999, Bolto et al. 2002a). The pore structure of resins can be characterized as either macroporous or gel-containing. Macroporous resins have a true pore phase with a measurable internal surface area, whereas gel-containing resins possess no permanent pores and have no measurable BET surface area (Fu and Symons 1990, Clifford et al. 1999). The classification of a resin as either a weak- or strong-base anion exchange resin is determined by the effective pH range of the resin (Clifford 1999). Weak-base resins are characterized by primary, secondary, or tertiary amine functional groups and can only be used in waters with a pH less than 6. Strong-base resins have quaternary amine functional groups. Since the quaternary amine is strongly basic, the nitrogen will be protonated, conveying a positive charge to the resin over the pH range 3 to 13. Most strong-base anion exchange resins are used in the chloride form (e.g. chloride ion is the counter-ion to the amine functional group) (Clifford 1999). In summary, macroporous strong-base anion exchange resins with an open structure and high water content perform best for NOM removal (Boening et al. 1980, Fu and Symons 1990, Clifford et al. 1999, Bolto et al. 2002a).

In water treatment, ion exchange resins are normally operated in a fixed-bed mode. The earliest literature on DBP control by anion exchange resins was a pilot-plant study using weak-base resins (Rook and Evans 1979). The results were promising with 70-85% reduction in chloroform formation potential and a 60% reduction in THMFP. Other researchers have verified that anion exchange resins can remove NOM and reduce subsequent THM formation (Brattebo et al. 1987, Kim and Symons 1991, Fettig 1999, Bolto et al. 2002b). In Norway, 13 ion exchange plants designed specifically to remove

NOM were built in the 1990s. The anion exchange process has proven to be competitive with processes such as enhanced coagulation and membrane filtration with respect to performance and economics (Odegaard et al. 1989, Hongve et al. 1999, Odegaard et al. 1999).

2.4.4.3 Magnetic Ion Exchange

A magnetic ion exchange resin developed by Orica Watercare of Victoria, Australia was designed specifically to remove DOC from natural water. The MIEX resin has traditional anion exchange properties, such as a polyacrylic matrix in the chloride form, a macroporous structure, and strong-base functional groups. In contrast to traditional anion exchange resins, the MIEX resin has magnetized iron oxide incorporated into the polymer matrix. The magnetic component aids agglomeration and settling of the resin, allowing the resin beads to be smaller so that they can be applied to raw water in a slurry form. The MIEX resin beads have a diameter of approximately 180 μm. The diameter of the MIEX resin is 2 to 5 times smaller than traditional ion exchange resins, resulting in an increase in the surface area to volume ratio and a decrease in the resistance to solid-phase mass transfer. Instead of being used in a fixed-bed like traditional ion exchange resins, MIEX is designed to be used in a suspended manner in a completely mixed flow reactor. This increases the turbulence around the resin and decreases resistance to liquid-phase mass transfer. Since the kinetics of ion exchange are governed by solid- and liquid-phase mass transfer, MIEX should remove NOM much faster than traditional ion exchange resins (Slunjski et al. 2002).

From the perspective of water treatment plant design, because the MIEX resin is used in slurry form, it can be used to treat raw water whereas traditional ion exchange units are typically placed after filtration to minimize fouling. The MIEX process starts with a raw water/MIEX slurry entering completely mixed flow reactors (i.e. contactors). In the contactors, the MIEX is mixed for 15-30 minutes. The slurry then enters a gravity settler/up-flow clarifier where the MIEX settles and is drawn off the bottom; the treated supernatant water overflows and proceeds to additional treatment. MIEX resin is dosed volumetrically (mL/L), with a recommended steady-state concentration in the contactor

of 20 mL/L to aid in settling. When the MIEX is drawn from the bottom of the gravity settler, 90-95% of the resin mass is recycled back to the contactor. The remaining 5-10% of the resin is diverted to a batch regeneration unit. Fresh (regenerated) resin is added to make-up for the resin diverted for regeneration and the resin is recycled back to the head of the process. Regeneration is achieved with a high concentration of sodium chloride brine. Pilot-plant studies have shown that 99.9% of the MIEX resin is recovered during settling, but a solid-liquid separation process, such as coagulation and settling, must follow MIEX treatment to remove any resin fines that carry-over, as well as turbidity from the raw water (Smith et al. 2002).

Bench-scale testing of MIEX resin, using doses of 5-10 mL/L, illustrated rapid rates of NOM removal, with the majority of UV-absorbing organics removed in the first 10-20 minutes (Singer and Bilyk 2002, Lee et al. 2002, Lee et al. 2003, Johnson and Singer 2003). MIEX treatment removed UV-absorbing organics to a greater extent than overall DOC. A further benefit of treatment with MIEX is that it has been shown to remove bromide (Singer and Bilyk 2002, Johnson and Singer 2003). Johnson and Singer (2003) showed that bromide removal by MIEX decreases with increasing alkalinity (i.e. carbonate concentration) and initial bromide ion concentration. MIEX has been shown to remove HPOA, TPHA, and HPIA fractions of NOM (Singer and Bilyk 2002, Lee et al. 2002, Lee et al. 2003). MIEX treatment also removes a wide range of molecular weight fractions. MIEX treatment has been shown to outperform enhanced coagulation with respect to removing UV-absorbing organics, DOC, THMFP, and HAAFP (Singer and Bilyk 2002, Drikas et al. 2003). MIEX also removes a wider range of organic acid fractions and molecular weight fractions than coagulation.

Pilot-plant evaluations of treatment with MIEX have corroborated bench-scale testing results. Bourke et al. (2002) showed that effluent from a MIEX pilot-plant had a lower DOC concentration than enhanced coagulation, and that the subsequent coagulant dose after treatment with MIEX was reduced. Meisch (2003) also verified, through pilot-plant studies, that MIEX was more effective than enhanced coagulation. Treatment with MIEX at the pilot-scale removed UV-absorbing organics > HAAFP > THMFP > DOC. Some bromide removal was also observed during pilot-plant testing. Bromide removal was dependent on alkalinity, other anions such as sulfate, and the type of salt used for

regeneration. Results from pilot-plant testing of MIEX verified the removal of a wide range of organic acid fractions and molecular weight fractions of organic matter (Meisch 2003)

There are two full-scale MIEX treatment plants in use for removing DOC from raw drinking water. The plants are located at Mt. Pleasant, South Australia and Wanneroo, Western Australia. The Mt. Pleasant Water Treatment Plant, constructed in 2001, is rated at 2.5 ML/d. Its water source is the River Murray, which is characterized by high turbidity, high DOC, and high color. Data from the MIEX treatment plant at Mt. Pleasant have shown DOC removal on the order of 40-50% (Slunjski et al. 2002). The Wanneroo Water Treatment Plant, rated at 112.5 ML/d, treats a highly colored, high DOC groundwater. The MIEX process was chosen both to remove DOC and help mitigate taste and odor associated with dimethyl trisulfide. During pilot-plant studies at Wanneroo, treatment with MIEX consistently removed 60% of the DOC and the brine regenerant was capable of being reused 10 times (Smith et al. 2002).

CHAPTER 3

MATERIALS AND METHODS

3.1 GENERAL APPROACH

Treatment with MIEX was evaluated for its effectiveness in removing DBP precursors from raw drinking water as compared to coagulation with alum. Four raw drinking waters with varying levels of TOC, UV absorbance, and bromide were chosen for this study. Upon receipt, samples of the raw water were taken for analysis of TOC, DOC, UV254, pH, alkalinity and turbidity. A portion of the raw water was set aside for bromide analysis, chlorination and subsequent THMFP and HAAFP analysis, XAD fractionation, and molecular weight fractionation. The remainder of the raw water was used for MIEX experiments, coagulation experiments, and studies with other ion exchange resins.

As shown in Figure 3.1, preliminary jar-test experiments were conducted using the raw water. Samples from the preliminary experiments with MIEX were analyzed for TOC, DOC, UV254, pH, and turbidity to determine an appropriate MIEX dose for subsequent treatment. A portion of the samples was set aside for bromide analysis. Approximately 15 L of raw water was then treated with the MIEX dose selected based on TOC, DOC, and UV254 results. Approximately 3 L of the batch MIEX-treated water was used for preliminary coagulation jar-test experiments to determine an appropriate alum dose based on turbidity removal. Six liters of batch MIEX-treated water was then coagulated at the alum dose selected. Preliminary coagulation jar-test experiments were conducted with each raw water to determine an appropriate alum dose based on turbidity, TOC, DOC, and UV254 removal. Approximately 4 L of coagulated raw water was then generated using the alum dose selected.

A series of experiments was also conducted to compare MIEX resin with several other anion exchange resins. The ion exchange resins were evaluated with respect to their capacity for NOM (as measured by DOC and UV254) and their rate of up-take of NOM. Seven-day isotherm studies were conducted to compare the capacities of the ion

exchange resins. In the isotherm studies, four to six doses of ion exchange resin were added to the raw water and continuously mixed for seven days. Samples from each resin dose were analyzed for DOC and UV254. Based on the isotherm study, one dose was chosen for all of the ion exchange resins to be used in the kinetic study. In the kinetic study, all resins were added at the same dose and then mixed for 2.5 minutes to 1 day. At pre-determined times, samples were taken off the mixer and analyzed for DOC and UV254. Samples from two contact times were also set aside for bromide analysis.

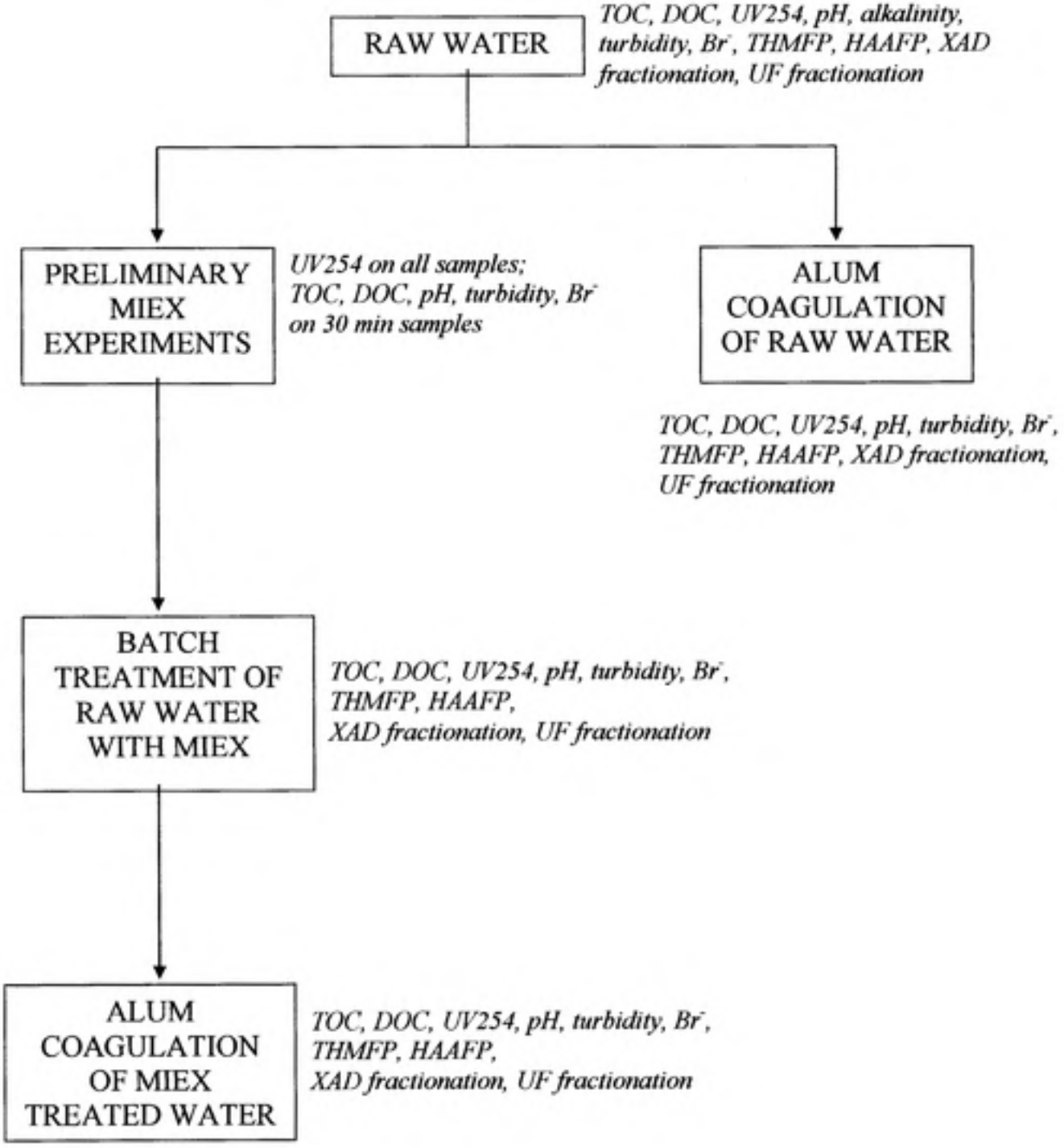

Figure 3.1 Schematic of general experimental approach

3.2 MATERIALS

3.2.1 Waters

Approximately 30 gallons of raw water from each sample location was shipped by overnight carrier to the Water and Wastewater Research Center at the University of North Carolina at Chapel Hill. The water was collected in 2.5 gallon plastic cubitainers and shipped with two cubitainers per cooler. Upon arrival the cubitainers were stored in a walk-in cooler at 4°C.

The four raw surface waters used in this research were chosen to represent a range of TOC and bromide concentrations and also different NOM characteristics in California. The four raw waters were from: North Bay Aqueduct (NBA), Castaic Lake (CL), South Bay Aqueduct (SBA), and Sweetwater Lake (SL). Table 3.1 provides a summary for each water. Prior to using the raw water in any experiments, the cubitainers were removed from the walk-in cooler and allowed to equilibrate to room temperature. The cubitainers were shaken vigorously to completely mix the raw water before use.

Table 3.1 Raw water source and location

Water	Date of Collection	Sample Location
NBA	March 18, 2003	North Bay Regional Water Treatment Plant located between Fairfield, CA and Vacaville, CA
CL	July 8, 2003	Castaic Lake in Santa Clarita Valley
SBA	August 24, 2003	Del Valle Water Treatment Plant in the Livermore-Amador Valley
SL	November 17, 2003	Blend of Sweetwater River water and Sweetwater Reservoir water

3.2.2 Glassware and Reagents

Glassware used for general experiments was first washed with detergent (Alconox Inc., NY) and warm tap water. The glassware was then rinsed with tap water at least six times to remove any detergent residue followed by at least three rinses with deionized

organic-free water (DOFW) (Dracor Inc., Durham, NC). The glassware was then air-dried overnight.

The DOFW was produced by passing tap water through a Dracor (Durham, NC) point-of-use water treatment system. The Dracor system consisted of a 1.0 μm pre-filter, 0.5 ft^3 of activated carbon, and two ion exchange beds. The activated carbon removed chlorine and organic matter while the ion exchange beds removed dissolved salts. The activated carbon and ion exchange beds were replaced approximately every six months.

Glassware used for TOC and DOC analysis was prepared following the general glassware cleaning procedure with the additional steps of soaking in a 10% nitric acid bath for at least twelve hours, rinsing three times with DOFW, and finally oven-drying at 180°C for at least twelve hours. The 50 mL TOC standard vials and 7 mL TOC sample vials were prepared in an identical fashion. Caps and septa were soaked in DOFW for twenty-four hours, rinsed three times with DOFW, and then air-dried.

Volumetric glassware (i.e. volumetric flasks, graduated cylinders, and volumetric pipettes) were prepared according to the general glassware procedure. These pieces of glassware were not subjected to acid or heat due to concerns about changing their calibrated volume.

Chlorine demand-free glassware was prepared by submerging glassware in a 100 mg/L (as Cl_2) sodium hypochlorite solution for at least three hours. The glassware was then rinsed three times with DOFW and air-dried. This glassware was only used for the chlorination experiments. Chlorine demand-free glassware was cleaned between experiments by rinsing three times with DOFW since it no longer had a chlorine demand. The following chlorine demand-free glassware was prepared: 100 mL volumetric flasks and glass stoppers, 300 mL BOD bottles and glass stoppers, beakers (50 and 100 mL), and volumetric pipettes (1, 2, 3, 4, 5, 6, 10, and 20 mL).

Clear 40 mL glass sample vials for THM and HAA analysis were soaked in a detergent tap water solution for twenty-four hours, rinsed six times with tap water, soaked in a 10% nitric acid bath for twenty-four hours, rinsed three times with DOFW, rinsed three times with methanol (Mallinckrodt Chemicals, Paris, KY), and oven-dried at 180°C for twenty-four hours. Screw caps and septa were soaked in DOFW for twenty-four hours, rinsed three times with DOFW, rinsed three times with methanol

(Mallinckrodt Chemicals, Paris, KY), and air-dried. All other THM and HAA glassware was rinsed three times with DOFW, rinsed three times with methanol (Mallinckrodt Chemicals, Paris, KY), and air-dried.

All reagents were ACS grade or higher.

3.2.3 Ion Exchange Resins

Orica Watercare of Englewood, CO provided the MIEX resin in slurry form in 500 mL plastic bottles. The bottles contained approximately 90% resin and 10% carrier water by volume. Upon delivery the contents of the containers were emptied into a 10 L Nalgene carboy (Nalge Company, Rochester, NY). For every 1 mL of resin added, 1 mL of DOFW was added to keep the resin from drying out. There was a spigot at the bottom of the 10 L carboy which allowed for easy withdrawal of the resin slurry.

In all experiments with MIEX, the resin was dosed volumetrically (mL resin/L water). To measure out a MIEX dose, the 10 L carboy was first shaken vigorously to suspend the MIEX resin. MIEX was then poured into a 10 mL glass graduated cylinder by opening the spigot at the bottom of the carboy. The MIEX was allowed to settle in the graduated cylinder and then more MIEX was either added or MIEX was removed to attain the desired volume. A disposable 5 ¾ in. glass Pasteur pipette (Fisher Scientific, Fair Lawn, NJ) was used to add/remove MIEX to/from the graduated cylinder. DOFW was added to the graduated cylinders to aid settling and to keep the resin saturated. The contents of the graduated cylinder were then added to the water sample being treated by rinsing the graduated cylinder with DOFW until all the MIEX resin was transferred.

The other anion exchange resins evaluated were: Ionac Macro-T (M-T), (Sybron Chemicals Inc., Birmingham, NJ); Ionac A641 (A641), (Sybron Chemicals Inc., Birmingham, NJ); SIR-22P-HP (SIR), (ResinTech Inc., Cherry Hill, NJ); Amberlite XAD761 (XAD761), (Rohm and Haas, Philadelphia, PA); and Amberlite XAD7HP (XAD7HP), (Rohm and Haas, Philadelphia, PA). The resins were received in a dry state from the manufacturer in plastic containers. Approximately 100 mL of dry resin was added to a 250 mL Erlenmeyer flask. DOFW was added to the resin to make a slurry. The resin was washed by suspending the resins in DOFW, allowing it to settle, and then

decanting the DOFW. This washing procedure was repeated at least ten times. The resin was stored in DOFW in a glass Erlenmeyer flask. The other ion exchange resins were measured volumetrically and dosed in an identical fashion to MIEX resin. Table 3.2 illustrates important physical and chemical properties of the MIEX resin and the other anion exchange resins evaluated.

Table 3.2 Physical and chemical properties of ion exchange resins

Resin	Size (mm)	Polymer Structure	Functional Group	Ionic Form	Water Content (%)
MIEX	0.18	Polyacrylic	Quaternary Amine	Cl^-	Not Available
SIR	0.3-0.85	Styrene-Divinylbenzene	Quaternary Amine	Cl^-	70-80
M-T	0.3-1.25	Acrylic-Divinylbenzene	Strong Base	Cl^-	60-64
A641	0.3-1.2	Styrene-Divinylbenzene	Quaternary Amine	Cl^-	54-58
XAD761	0.56-0.76	Phenol-Formaldehyde	Phenol	non-ionic	62-70
XAD7HP	0.56-0.71	Aliphatic Acrylic	None	non-ionic	61-69

3.3 EXPERIMENTAL PROCEDURES

3.3.1 Coagulation Experiments

Preliminary coagulation jar-test experiments were conducted with aluminum sulfate ($Al_2(SO_4)_3 12\text{-}14H_2O$), alum (Fisher Scientific, Fair Lawn, NJ). The coagulation protocol entailed rapid mixing at 100 rpm for 1 minute, slow mixing at 35 rpm for 20 minutes, and quiescent settling for 30 minutes. Four to six alum doses, chosen based on the raw water characteristics, were evaluated during the preliminary coagulation jar-tests. A 1,000-2,000 mg/L alum dosing solution was prepared by weighing the appropriate amount of alum using an Ohaus AR2140 analytical balance (Ohaus Corp., Pine Brook, NJ) and adding the alum to a 1 L volumetric flask which was filled to the line with DOFW. A magnetic stir bar was used to agitate the solution to ensure dissolution of all of the alum. Five hundred milliliters of the water sample was added to 600 mL glass beakers with a sampling port positioned 3 in. below the top of the beaker. The beakers were then mixed using a Phipps and Bird (Richmond, VA) six paddle stirrer. The rectangular stainless steel paddles were 2 in. by 1 in.

Two Phipps and Bird (Richmond, VA) six paddle stirrers were used during the coagulation experiments, one for rapid mixing and the other for slow mixing. The 600 mL beaker containing the water sample was placed under the *rapid mixing* paddle stirrer and mixed at 100 rpm by adjusting the speed controller. Based on the concentration of the alum dosing solution, the appropriate volume of alum solution was transferred to the sample using a volumetric pipette. The lowest alum dose was added to the first jar. A timer was then started and, after 1 minute of rapid mixing, the sample was transferred to the *slow mixing* paddle stirrer. When the beaker was placed under the slow mixing paddle stirrer and the speed adjusted to 35 rpm, a second timer was started. This procedure was repeated at approximately three minute intervals making note of the time each alum dose started slow mixing.

After 20 minutes of slow mixing, the paddle was lifted out of the jar and the sample was allowed to settle undisturbed for 30 minutes. Following 30 minutes of quiescent settling, the supernatant was withdrawn from the beaker into a 250 mL Erlenmeyer flask using the sampling port. The first 10-20 mL of sample was always discarded. A sample was taken for measurement of turbidity. Approximately 100 mL of sample was vacuum-filtered through 0.45 μm membrane filter paper (Supor-450, Pall Corp., Ann Arbor, MI) which had been pre-rinsed with 500 mL of DOFW and 10-20 mL of sample. The filtered sample was analyzed for DOC and UV254. The pH of the unfiltered sample was measured and the sample was analyzed for TOC. All samples were stored in 250 mL Erlenmeyer flasks covered with aluminum foil and refrigerated at 4°C.

The criteria for choosing an appropriate alum dose were based primarily on turbidity removal, but TOC removal was also considered. For coagulation, the PODR is the point at which a 10 mg/L increase in the alum dose results in less than 0.3 mg/L of TOC removal (Krasner and Amy 1995). The appropriate alum dose had to lower the turbidity to below 2 NTU and be less than the PODR alum dose. Once the desired alum dose was established, a bulk coagulation experiment at the alum dose selected was performed to generate enough coagulated water to perform a series of other experiments. The bulk coagulation experiments were identical to the preliminary coagulation experiments except that 2 L square jars (Phipps and Bird Inc., Richmond, VA) fitted with

a sampling port located 4 in. below the fill line and 3 in. by 1 in. rectangular stainless steel paddles were used. Approximately 3 L of treated water was then pressure-filtered through a 0.45 μm nitrocellulose membrane (Millipore Corp., Bedford, MA). The filtration set-up consisted of a 4 L stainless steel pressure-vessel which fed a 350 mL ultrafiltration cell (Millipore Corp., Bedford, MA). Nitrogen gas was used to pressurize the vessel and force the water through the membrane filter. The membrane was pre-filtered with 500 mL of DOFW. The filtered water was collected in a 4 L Erlenmeyer flask. Both unfiltered and filtered bulk coagulated samples were stored in a walk-in cooler at 4°C.

3.3.2 Experiments with MIEX

Preliminary experiments with MIEX were performed on each raw water to evaluate the impact of MIEX treatment on raw water parameters such as turbidity, TOC, DOC, bromide, and UV254. MIEX doses in the range of 1-6 mL/L were tested based on the raw water characteristics and previous research by Singer and Bilyk (2002). In the preliminary experiments with MIEX, samples were dosed with MIEX as described above, rapid mixed for 30 minutes at 100 rpm, and then allowed to settle for 30 minutes. The MIEX procedures followed were based on the previous research of Singer and Bilyk (2002).

Two liters of the water to be tested was added to 2 L square jars (Phipps and Bird Inc., Richmond, VA) fitted with a sampling port. The square jars were placed under a Phipps and Bird (Richmond, VA) six-paddle stirrer equipped with 3 in. by 1 in. rectangular stainless steel paddles. The lowest MIEX dose was then added to the first jar, the speed was adjusted to 100 rpm, and a timer was started. This procedure was repeated approximately every two minutes until all of the jars had been dosed with MIEX. The lowest MIEX dose was always added to the first jar. While mixing, 50 mL samples were taken at 5, 10, and 20 minutes for UV254 analysis. The samples were vacuum-filtered through 0.45 μm membrane filter paper according to the procedure described previously and stored in 250 mL Erlenmeyer flasks covered with aluminum foil and refrigerated at 4°C. After mixing for 30 minutes and settling for 30 minutes, a final sample was taken

which was measured immediately for turbidity and later for TOC, DOC, and UV254. UV254 was plotted against time for each MIEX dose to determine the most appropriate mixing time. UV254 consistently plateaued after 20 minutes of mixing, independent of dose or sample water. Similar results were also found by Singer and Bilyk (2002). The appropriate MIEX dose for each water was chosen based on DOC and UV254 removal.

Bulk MIEX experiments were conducted using a mixing time of 20 minutes and the MIEX dose determined from the preliminary MIEX jar-test experiments. A 15 L glass carboy with a stainless steel paddle mixer that screwed on top was used for the bulk MIEX experiments. The 15 L glass carboy was fitted with a sampling port located 6 in. above the bottom of the container. The rectangular stainless steel paddle was 8 in. by 1 ¼ in. and was designed to transfer an equivalent amount of energy to the water as the 3 in. by 1 in. mixing blade transferred to the water in the 2 L square jars. The 15 L carboy was filled with 14 L of water. Several 10 mL glass graduated cylinders were filled with MIEX to achieve the necessary volume of MIEX to be transferred. The MIEX was added to the carboy, the mixer screwed on top of the carboy, and the contents of the carboy were mixed at approximately 100 rpm for 20 minutes. After mixing, the sample was allowed to settle for 30 minutes. Using the sampling port, the first 50 mL of sample was discarded, then approximately 12 L of supernatant was decanted into a 20 L Nalgene carboy (Nalge Company, Rochester, NY). Four liters of treated water was pressure-filtered through a 0.45 μm membrane filter. The filtered water was collected in a 4 L Erlenmeyer flask. Both unfiltered and filtered MIEX-treated samples were stored in a walk-in cooler at 4°C.

A quality control experiment was conducted with the first water to ensure that all aspects of the MIEX experimental plan were reproducible. Five hundred milliliters of the test water was added to six 600 mL beakers fitted with a sampling port and placed under a Phipps and Bird (Richmond, VA) six-paddle stirrer with 2 in. by 1 in. rectangular stainless steel paddles. Following the procedure detailed above, 4 mL of MIEX resin was measured out into six 10 mL glass graduated cylinders. The MIEX was then transferred to the jars and the samples mixed according to the jar-testing procedure outlined above. After vacuum-filtering the samples through a 0.45 μm membrane filter, they were analyzed for DOC and UV254. The coefficient of variation (i.e. the standard deviation

divided by the mean) was less than 10% for TOC, DOC, and UV254. The results are included in Appendix A.

3.3.3 Experiments with MIEX and Coagulation

Unfiltered MIEX-treated water was coagulated with alum following the preliminary coagulation jar-test procedure. An appropriate alum dose was then chosen based on the same turbidity and TOC criteria stated above. Since some of the raw waters had a low initial turbidity, the turbidity following treatment with MIEX was near 2 NTU. For these waters, the alum dose was also based on qualitative experimental observations such as floc formation and floc settleability. Coagulation was then conducted using this appropriate alum dose with the MIEX-treated water following the coagulation procedure discussed above. Approximately 4 L of the MIEX-treated coagulated water was generated. Three liters of this treated water was pressure-filtered through a 0.45 μm membrane filter and transferred to a 4 L Erlenmeyer flask. Both the filtered and unfiltered MIEX-treated coagulated water were stored in a walk-in cooler at 4°C until future use.

3.3.4 Experiments with Other Ion Exchange Resins

Two types of experiments were conducted in order to compare the performance of various ion exchange resins examined: a seven-day isotherm study and a short-term kinetic experiment. The set-up for both experiments was identical. Twenty-four approximately 250 mL square French jars with screw caps were filled with 250 mL of raw water. The ion exchange resins were measured out as described in § 3.2.3 using plastic graduated micro-centrifuge tubes. Two sizes of micro-centrifuge tubes were employed: a 1.5 mL tube with 0.5 mL graduations and a 0.6 mL tube with 0.2 mL graduations. The resins were then transferred to their respective French jars using DOFW.

For the isotherm studies, resin doses of 1-6 mL/L were evaluated. For the kinetic studies, a uniform resin dose based on the isotherm study for that raw water was dosed for all resins. The French jars were then inserted into cylindrical holders and secured with tape on a twenty-four place rotary mixer. For the isotherm study, the French jars containing raw water and resin were continuously mixed for seven days. After seven days of mixing, the jars were removed from the mixer and approximately 150-200 mL of sample was vacuum-filtered through a pre-rinsed 0.45 μm membrane filter (Supor-450, Pall Corp., Ann Arbor, MI). The filtered samples were transferred to 250 mL Erlenmeyer flasks and were analyzed for DOC and UV254. For the kinetic studies, a timer was started and the French jars containing raw water and resin were mixed for time increments ranging from 2.5 minutes to 1 day. At pre-determined times, the mixer was stopped, and one French jar per resin was removed. Approximately 150-200 mL of sample was immediately vacuum-filtered through a pre-rinsed 0.45 μm membrane filter (Supor-450, Pall Corp., Ann Arbor, MI) as outlined above. The filtered samples were transferred to 250 mL Erlenmeyer flasks and were analyzed for DOC and UV254. Two samples for each resin treatment were also analyzed for bromide. All samples from both the isotherm and kinetic studies were stored at 4°C.

3.3.5 Chlorine Demand and Chlorination under Uniform Formation Conditions

A 4-6% NaOCl solution (Fisher Scientific, Fair Lawn, NJ) was the stock solution used for all chlorination experiments. The stock NaOCl solution bottle was wrapped in aluminum foil and stored at 4°C to limit degradation. The chlorination procedure employed uniform formation conditions (UFC) as described by Summers et al. (1996). The UFC were those conditions that yielded a 1 mg/L free chlorine residual as Cl_2 at pH 8 after 24 hours of incubation in the dark at 20°C. Before every chlorination experiment, a 1,000-3,000 mg/L chlorine working solution was prepared and was titrated with standard sodium thiosulfate ($Na_2S_2O_3$) to verify its strength (see below). An Excel spreadsheet was created to interpret the titration results and determine the volume of working solution needed to make 100 mL of a 100 mg/L as Cl_2 dosing solution. The chlorine dosing solution was prepared in a 100 mL volumetric flask by adding a 4-5:1

volume ratio of working solution to pH 6.7 borate buffer. The flask was then filled to the line with DOFW and inverted three times. All glassware used in chlorination experiments was chlorine demand-free as described in § 3.2.2.

After the chlorine dosing solution was prepared, a DOFW test was conducted to verify its strength. Since the chlorine dosing solution had a strength of 100 mg/L as Cl_2 and the samples were in 100 mL volumetric flasks, the volume of chlorine dosing solution added was equivalent to the dose in mg/L as Cl_2. Volumetric pipettes were used to transfer the chlorine dosing solution. A 100 mL volumetric flask was filled half-full with DOFW, 0.2 mL pH 8 borate buffer, 1 mL of chlorine dosing solution, and then filled to the line with DOFW. The volumetric flask was inverted three times. The free chlorine residual and pH were measured following the procedures outlined below. If the free chlorine residual of the DOFW was not 1 ± 0.2 mg/L as Cl_2, the dosing solution was discarded and a fresh solution prepared. The stock 4-6% NaOCl solution had to be replaced once due to significant degradation.

For the chlorine demand experiments, four to five doses of chlorine (1-2 mg Cl_2 per mg DOC) were evaluated per water. All water samples were previously vacuum-filtered or pressure-filtered through a 0.45 μm membrane filter. One hundred milliliter volumetric flasks were filled with approximately 75 mL of sample, 0.2 mL pH 8 borate buffer, and the desired chlorine dosage. The volumetric flasks were then filled to the line with sample, inverted three times, and incubated in the dark for 24 hours at 20°C. Two volumetric flasks containing DOFW dosed with 1 mL of dosing solution and 0.2 mL of pH 8 borate buffer were also incubated with the samples and measured with the samples to confirm that the DOFW did not exert a chlorine demand. Chlorine residuals were measured after 24 hours.

The objective of the chlorine demand experiments was to determine, for a given water, the chlorine dose necessary to yield a free chlorine residual of 1 mg/L as Cl_2 at pH 8 after 24 hours. After determining the requisite chlorine dosage, 300 mL glass-stoppered BOD bottles were used to chlorinate a larger volume of sample water to be used for THM and HAA analysis, following the above procedure. The BOD bottles were filled headspace-free and incubated in the dark at pH 8.0 for 24 hours at 20°C. After 24 hours, the free chlorine residual and pH were measured as detailed below.

Samples chlorinated under UFC for THM and HAA analysis were transferred to 40 mL glass vials with screw caps and polytetrafluoroethylene (PTFE)-lined silicone septa (Laboratory Supply Distributors Corp., Mt. Laurel, NJ). The samples were poured down the side of the vial to minimize air interactions and filled headspace free. Each vial contained 20 mg of ammonium sulfate ($(NH_4)_2SO_4$) (Mallinckrodt Chemicals, Paris, KY), which quenched the chlorine residual and stopped further production of DBPs. THM sample vials also contained 0.7 g of phosphate buffer (Sigma Aldrich Chemical, Milwaukee, WI) to standardize the pH of the sample between 4.8 and 5.5. HAA sample vials also contained 50 µL of 80 mg/L sodium azide solution (NaN_3) (Aldrich Chemical Co., Milwaukee, WI) which was employed as a biocide. All samples were collected in duplicate, stored at 4°C, and extracted within three weeks of chlorination.

3.3.6 Characterization of NOM

NOM was separated into HPOA, TPHA, and HPIA fractions using an XAD resin technique and into molecular weight fractions using an ultrafiltration technique. Amberlite XAD-8 and XAD-4 resins (Rohm and Haas, Philadelphia, PA) were used to fractionate raw and treated water samples following procedures outlined by Thurman and Malcolm (1981) and Aiken et al. (1992). The fractionation set-up consisted of a glass column packed with 12 mL of XAD-8 resin followed by a second glass column packed with 12 mL of XAD-4 resin. Before each use, both the XAD-8 and XAD-4 columns had to be cleaned by pumping 0.1 N NaOH at 4 mL/min for 10 minutes followed by 0.1 N HCl at 4 mL/min for 10 minutes through the columns. This cleaning process was repeated three times. The sample to be fractionated was first filtered through a 0.45 µm membrane filter as described above. The sample was then acidified with concentrated HCl (Fisher Scientific, Fair Lawn NJ) to below pH 2 to ensure all functional groups on the NOM would be protonated. One liter of sample was then measured using a 1 L volumetric flask. After the cleaning process was complete, the sample was pumped through the top of the column at 4 mL/min. The first 12 mL (i.e. one bed volume) of effluent from the column was discarded and then the rest of the sample was collected in a 1 L amber glass bottle with screw cap. The raw water was first passed through the XAD-

8 column then on the next day the XAD-8 effluent was passed through the XAD-4 column. The HPOA fraction was retained on the XAD-8 column, the TPHA fraction was retained on the XAD-4 column, and the HPIA fraction passed through both columns. The concentration of DOC of the sample water and the effluent from each column was measured and the concentration of DOC of each fraction was calculated by difference (e.g. the DOC concentration of the HPOA fraction was equal to the difference in the DOC concentrations of the influent sample and the XAD-8 effluent).

The time was monitored for all runs to ensure the pumping rate remained approximately constant at 4 mL/min. The sample was pumped through the top of the column until the water level was just above the resin bed. Once the water level was just above the resin the pump was stopped. The column was then back-eluted by pumping 0.1 N NaOH up through the bottom of the column. Two 100 mL eluate samples were collected in 100 mL glass graduated cylinders and transferred to 100 mL amber glass bottles with screw caps. The eluate samples were then acidified with concentrated HCl to pH less than 2. The DOC concentration of the back-eluted sample was used as a check for the DOC concentration of the fractions (e.g. the mass of DOC in the XAD-8 eluate should equal the difference in the mass of DOC in the XAD-8 influent and effluent). Once the column had been back-eluted, the column was acidified with 0.1 N HCl until the pH of the effluent was acidic.

Approximately 50-100 mL of XAD-8 effluent was transferred to a 100 mL amber glass bottle with screw cap. The volume of the XAD-8 effluent was measured using a 1 L glass graduated cylinder. The XAD-8 effluent was then pumped through the top of the XAD-4 column following the above procedure. All samples were analyzed for DOC and UV254. For sample waters with a high concentration of TOC, the back-eluted samples had to be diluted prior to TOC analysis.

The molecular weight distribution of the raw water and treated waters was determined by ultrafiltration. Samples of raw water and treated water were filtered, in parallel, through membranes with a 1,000, 10,000, and 30,000 Dalton nominal molecular weight cutoff. This yielded four fractions with apparent molecular weights (AMWs) of less than 1,000 Daltons (<1k), 1,000-10,000 Daltons (1-10 k), 10,000-30,000 Daltons (10-30 k), and greater than 30,000 Daltons (>30k) (Millipore Corporation, Bedford, MA).

It should be noted that ultrafiltration cannot provide absolute molecular weight values, but is useful operationally for making comparisons.

The ultrafiltration membranes were received with pretreatments of glycerin to prevent drying and sodium azide as a preservative. To remove the preservatives, the membranes were floated face down in 25 mL of a 10% sodium chloride solution for 30 minutes. The membranes were then rinsed with DOFW by suspending the membranes in 500 mL beakers filled with approximately 200 mL of DOFW. The water was changed every 20 minutes for one hour. Each membrane was inserted into a 350 mL stirred ultrafiltration cell (Millipore Corporation, Bedford, MA). The cell was pressurized with nitrogen gas and operated at 55 psi. Seventy milliliters of DOFW was filtered through each membrane.

Once the cleaning process was complete, 100 mL of sample water was transferred to the ultrafiltration cell. Approximately 70 mL of sample was filtered through each ultrafiltration membrane. The effluent was collected in a 100 mL amber glass bottle with screw cap. The volume remaining in the ultrafiltration cell was measured using a 50 mL glass graduated cylinder, and the filtered volume was calculated by difference. The whole water and filtered fractions were stored at 4°C until analyzed for UV254 and DOC. The DOC concentration of the four molecular weight fractions was calculated by difference.

3.4 ANALYTICAL METHODS

3.4.1 Ultraviolet Absorbance

UV254 was measured using a 1 cm quartz cell on a Hitachi U-2000 spectrophotometer (Hitachi Instruments Inc., Danbury CT) following Standard Method 5910 (Standard Methods 1998). The instrument was allowed to warm up for 30 minutes before samples were measured. Samples for UV254 analysis were either vacuum- or pressure-filtered through 0.45 μm membrane filters, as described above. The instrument was zeroed using DOFW. Between samples, the quartz cell was rinsed three times with

DOFW and once with the sample to prevent contamination. Samples were also analyzed from low to high absorbance, when possible, to help reduce contamination. When multiple samples were being analyzed, the absorbance of a DOFW blank was measured after every five to ten samples to make sure the instrument was still zeroed.

3.4.2 TOC and DOC Measurements

TOC and DOC were measured using a Shimadzu 5000 Total Organic Carbon Analyzer (Shimadzu Corp., Atlanta, GA) equipped with an ASI 5000 auto-sampler. DOC was operationally defined as the organic carbon concentration of a sample filtered through a membrane filter with a 0.45 μm pore diameter. Standard Method 5310B High-Temperature Combustion (Standard Methods 1998) was followed except that hydrochloric acid was used to acidify samples instead of phosphoric acid as recommended by the instrument manufacturer. The high-temperature combustion method employed measured non-purgeable organic carbon, with a lower detection limit of 0.5 mg-C/L and an upper limit of 10 mg-C/L.

A 1,000 mg-C/L stock solution was prepared by adding 2.128 g of potassium hydrogen phthalate ($HOCOC_6H_4COOK$) (Fisher Scientific, Fair Lawn, NJ) to a 1 L volumetric flask and filling to the line with DOFW. One hundred milliliters of stock solution was transferred to a 100 mL volumetric flask and stored at 4°C. From the stock solution, a 100 mg-C/L working solution was prepared by pipetting 10 mL of the stock solution into a 100 mL volumetric flask and filling to the line with DOFW. The working solution was stored at 4°C. Both the stock and working solutions were used for up to three months. On the day of analysis, three calibration standards were made from the working solution. The concentrations of the calibration standards were chosen to best bracket the suspected organic carbon concentration range of the sample. A low calibration point of 0.5 mg-C/L was always used. Calibration standards and samples were transferred to 50 mL and 7 mL TOC-free vials, respectively, and loaded on the auto-sampler. The calibration standards and samples were acidified with 2 N HCl (Fisher Scientific, Fair Lawn, NJ) to pH less than 2 to convert all inorganic carbon to CO_2. The

samples were then purged with ultra zero air (Holox Co, Morrisville, NC) for five minutes to drive out the CO_2.

The first one to three samples were DOFW blanks to prevent contamination from the highest standard to the first samples. After every ten samples, a DOFW blank and the lowest calibration standard were inserted to verify the calibration. If more than approximately 30 samples were analyzed, the instrument was recalibrated with the original standards. At the end of the run, a DOFW blank and the three calibration standards were measured as unknowns to verify that the instrument maintained its calibration. The squared correlation coefficient (R^2) for the calibration curve was calculated after every analysis, usually yielding a value greater than 0.99. If the R^2 of the calibration curve was less than 0.99 or if the check standards were not within ±0.2 mg/L of their expected concentration, the samples were reanalyzed.

3.4.3 pH

The pH was measured using an Accumet 10 pH meter with an Accumet pH probe (Fisher Scientific, Fair Lawn, NJ). The instrument was calibrated daily with pH 4, 7, and 10 buffer solutions (Fisher Scientific, Fair Lawn, NJ). A two-point calibration was performed with the pH 7 and 10 buffers, and then the calibration was checked with the pH 4 buffer. Potassium chloride solution (KCl) (Fisher Scientific, Fair Lawn, NJ) was added to the pH probe when the electrolyte solution fell below ¼ in. of the cap. All samples were stirred with a magnetic stir bar while measuring the pH to ensure a more accurate measurement.

3.4.4 Turbidity

Turbidity was measured using 30 mL glass sample vials with screw caps on a Hach Ratio Turbidimeter Model 18900 (Hach Co., Loveland, CO). The instrument had three operating ranges: 0-2 NTU, 0-20 NTU, and 0-200 NTU. The instrument was allowed to warm up for 15 minutes prior to sample measurement. The instrument was

calibrated every 60 days, or sooner if needed, using stabilized formazin primary turbidity standards (Hach Co., Loveland CO). The calibration procedure entailed adjusting the zero, span, and linearity controls. Selecting the 2 NTU range, with the sample cell holder empty and the light shield over the sample cell, the zero control was adjusted to obtain 0.00 on the display. Selecting the 20 NTU range, a sample containing an 18 NTU standard was inserted into the sample cell holder and covered with the light shield. The span control was adjusted to obtain 18.0 on the display. Selecting the 200 NTU range, a sample containing an 180 NTU standard was inserted into the sample cell holder and covered with the light shield. The linearity control was adjusted to obtain 180 on the display. Prior to each use, the calibration was checked using 1.8 NTU, 18 NTU, and 180 NTU Gelex standards (Hach Co., Loveland CO). If the turbidity of the Gelex secondary turbidity standards did not fall within 5% of its value, the instrument was recalibrated following the above procedure. When measuring a sample, the lowest possible turbidity range was used. The sample vials were rinsed three times with DOFW and once with the sample to prevent contamination.

3.4.5 Alkalinity

Alkalinity was measured following Standard Method 2320 Titration Method (Standard Methods 1998). Fifty milliliters of sample was added to a 100 mL beaker which was stirred using a magnetic stir bar. Six drops of bromcresol green – methyl red alcoholic solution (LabChem Inc., Pittsburgh, PA) was added to the sample using a disposable 9 in. glass Pasteur pipette. The sample was then titrated with 0.02 N standard sulfuric acid solution (H_2SO_4) (Fisher Scientific, Fair Lawn, NJ) using a 10 mL burette. The sample was titrated from green to pink. The alkalinity titration was performed at least three times per raw water; the reported alkalinity was the average of the three values.

3.4.6 Bromide

Samples to be analyzed for bromide were stored at 4°C until ready for analysis. Bromide samples were sent by overnight carrier to MWH Laboratories in Monrovia, CA in 50 mL plastic bottles without any preservatives and packaged in coolers with ice packs. MWH Laboratories conducts its bromide analysis using ion chromatography (IC) in accordance with EPA Method 300.0 (Radke, 2004).

A brief outline of the IC analysis procedure is as follows. The water sample is injected into a stream of carbonate/bicarbonate eluent and passed through a column packed with ion exchange resin. The anions are separated by the ion exchange resin based on the affinity of the resin for that particular anion. The separated anions are then converted to their highly conductive acid form (i.e. HBr) and the carbonate/bicarbonate eluent is converted to carbonic acid (low conductivity). The separated anions in their acid form are then detected by conductivity. Anion identification and concentration are based on retention times of known standards. MWH Laboratories has a minimum reporting level for bromide of 0.020 mg/L. No check standards or matrix spikes were sent to MWH laboratories because the author relied on their quality control and quality assurance protocols.

3.4.7 Chlorine Residual

The strength of the 4-6% NaOCl stock solution was determined before each use in accordance with Standard Method 4500-Cl B Iodometric Method I (Standard Methods 1998). A 1,000-3,000 mg/L as Cl_2 working solution was made from the 4-6% NaOCl solution in a 100 mL chlorine demand-free volumetric flask, and titrated by the following procedure to determine the exact strength of the working solution and to make sure the stock solution had not deteriorated. Forty milliliters of working solution was transferred to a 50 mL chlorine demand-free beaker with a magnetic stir bar for agitation. The pH of the sample was adjusted to between pH 3-4 using glacial acetic acid ($C_2H_4O_2$) (Fisher Scientific, Fair Lawn, NJ). One gram of granular potassium iodide (KI) (Fisher Scientific, Fair Lawn, NJ) was weighed out using an Ohaus AR2140 analytical balance

(Ohaus Corp., Pine Brook, NJ) and added to the sample. The sample was then titrated to pale yellow using 0.1 N standard sodium thiosulfate solution (Fisher Scientific, Fair Lawn, NJ). One milliliter of soluble starch solution (Fisher Scientific, Fair Lawn, NJ) was added to the sample to make end-point detection more precise. The sample was titrated to clear using additional 0.1 N standard sodium thiosulfate solution. The strength of the working and stock solutions were determined based on the volume of sodium thiosulfate required for the titration.

To measure the low level chlorine residuals from the chlorination experiments, a Hach Chlorine Pocket Colorimeter (Hach Co., Loveland, CO) was employed. The instrument consisted of a colorimeter and a 20 mL sample vial with screw cap. To measure the free chlorine residual, the sample vial was filled with 10 mL of sample as marked on the vial. The vial was wiped free of any residue and then inserted into the sample cell holder and covered with the light shield. The instrument was zeroed. One packet of DPD Free Chlorine Reagent (Hach Co., Loveland, CO) was added to the sample and shaken vigorously for 20 s. The sample vial was returned to the sample cell holder and covered with the light shield. After one minute, the free chlorine residual was read from the instrument in units of mg/L as Cl_2. The instrument had an upper bound of 2.2 mg/L as Cl_2, so for higher free chlorine residuals the samples were diluted appropriately using chlorine demand-free volumetric flasks and DOFW. Between samples, the sample vial was rinsed three times with DOFW and once with the sample to prevent contamination.

3.4.8 THM Analysis

The samples generated by chlorination under UFC were analyzed for THM4. Analysis was done by liquid-liquid extraction and gas chromatography with electron capture detection. The standard operating procedure followed was a modification of procedures published by the USEPA (EPA Method 551.1 1995) and the American Public Health Association (Standard Method 6232B 1998).

Individual THM (Cl_3CH, $BrCl_2CH$, Br_2ClCH, and Br_3CH) stock standards (Supelco, Bellefonte, PA) and 1,2-dibromopropane neat standard (Sigma Aldrich,

Milwaukee, WI) arrived in 1 mL sealed amber glass ampules. The glass ampules were opened and the contents transferred to 5 mL amber vials with screw caps and PTFE-lined silicone septa. The necks of the vials were wrapped with PTFE tape and stored in the laboratory standards freezer at -15°C. Certificates of Analysis of all stock standards were kept on file. THM stock standards were not used for more than six months after opening of the sealed ampules.

Individual THM working standards were prepared as a 1:5 dilution of the stock standard by adding 400 µL of each stock standard to 2 mL of Burdick & Jackson (Muskegon, MI) high purity methanol for THM analysis. The standards were injected directly into the methanol solvent using a micro-pipetter. The volumetric flasks were then filled to the line with methanol, capped, inverted three times, transferred to 5 mL amber glass vials with screw caps and PTFE-lined silicone septa, the neck of the vial wrapped with PTFE tape, and stored at -15°C. All THM working standards had a concentration of 1,000 µg/L.

An internal standard (IS) stock solution (IS-1°) was prepared by injecting 5 µL of 1,2-dibromopropane neat standard into a 5 mL volumetric flask containing methyl tert-butyl ether (MtBE) (Sigma Aldrich Chemical, Milwaukee, WI). The flask was then filled to the line with MtBE, stoppered, and inverted three times. The solution was transferred to a 5 mL amber glass vial with screw cap and PTFE-lined silicone septa, the neck of the vial wrapped with PTFE tape, and stored at -15°C. An IS secondary dilution (IS-2°) was prepared by injecting 250 µL of IS-1° into a 5 mL volumetric flask containing MtBE. The flask was filled to the line with MtBE, stoppered, and inverted three times. The solution was transferred to a 5 mL amber glass vial with screw cap and PTFE-lined silicone septa, the neck of the vial wrapped with PTFE tape, and stored at -15°C.

From the individual working standards, two primary calibration standards were prepared (calibration standard #1 and calibration standard #2). Both calibration standards were prepared in Burdick & Jackson (Muskegon, MI) high purity methanol for THM analysis. The standards were transferred to 5 mL amber glass vials with screw caps and PTFE-lined silicone septa, the neck of the vial wrapped with PTFE tape and stored at -15°C. THM calibration check standards were prepared from calibration standards #1 and #2 to verify they were prepared properly. The THM calibration check standards

were prepared in MtBE (Sigma Aldrich Chemical, Milwaukee, WI) plus IS-2°, transferred to clear glass autosampler vials capped with an aluminum-PTFE faced seal (Laboratory Supply Distributors Corp., Mt. Laurel, NJ), and analyzed on a Hewlett-Packard model 5890 series A Gas Chromatograph (GC). The primary calibration standards were monitored routinely for degradation and contamination by comparing standard area values to those obtained from the initial calibration check standards. Fresh standards were prepared if there was a drift of greater than 20% in the responses.

THM calibration test mixtures were prepared from calibration standards #1 and #2 a few days prior to sample extraction to verify that the calibration standards had not degraded. The THM test mixtures were prepared in an identical fashion to the THM calibration check standards. The test mixture responses were compared to those responses obtained when the calibration check standards were freshly prepared. A drop in response of greater than 20% was grounds for preparation of fresh calibration standards.

A small volume of the MtBE (Sigma Aldrich Chemical, Milwaukee, WI) plus IS-2° extraction solution was also prepared a few days prior to analysis and run on the GC to ensure the IS-2° or the solvent was not contaminated. If the IS response was not within ±10% of past values, a fresh IS-2° was prepared.

On the day of analysis, the 40 mL sample vials were removed from the refrigerator and allowed to reach room temperature. While the samples were equilibrating to room temperature, seven calibration standards were prepared from THM calibration standards #1 and #2. The calibration standards were prepared by injecting calibration standard #1 or #2 into DOFW in a 100 mL volumetric flask. Using a 25 mL glass graduated cylinder, a 20 mL aliquot of sample was measured out from the 40 mL sample vials and 100 mL calibration standard volumetric flasks. The samples were poured down the side of the graduated cylinder to reduce air volatilization. Between calibration standards and samples, the graduated cylinder was rinsed three times with DOFW and once with 5-10 mL of sample to minimize contamination.

Based on the number of calibration standards and samples to be analyzed, a pre-determined volume of MtBE plus IS-2° (MtBE/IS-2°) solution was prepared by adding 1 µL of IS-2° for every 1 mL of MtBE (Sigma Aldrich Chemical, Milwaukee, WI). The

solution was prepared in a volumetric flask and transferred to a 1 L amber bottle with a screw cap fitted with a pump pipette dispenser. Four milliliters of MtBE/IS-2° solution was added to each 20 mL aliquot of sample/calibration standard. Approximately 6 g of pre-baked sodium sulfate (Na_2SO_4) (Mallinckrodt, Paris, KY) was added to each 20 mL aliquot containing the MtBE/IS-2° solution. The salt was measured in a pre-marked 10 mL glass beaker. The salt was added to increase the effectiveness of the extraction process. After addition of the salt, the sample vial was Vortex-mixed (Type 16700 Mixer-MaxiMix I, Thermolyne, Dubuque, IA) for one minute. The samples were then allowed to settle for five minutes to allow any undissolved salt crystals to settle to the bottom and to allow the two liquids to separate. Two layers were then formed, an organic top layer (MtBE) and an aqueous bottom layer.

A 9 in. glass Pasteur pipette (Fisher Scientific, Fair Lawn, NJ) was employed to transfer 1.5 mL of the organic layer to a clear glass autosampler vial capped with an aluminum-PTFE faced seal (Laboratory Supply Distributors Corp., Mt. Laurel, NJ). Each sample was vialed in duplicate. The extracts were stored at -15°C until analyzed.

The extracts were analyzed on a Hewlett-Packard model 5890 series A GC with electron capture detector (ECD) and autosampler/autoinjector tower (Hewlett-Packard Co., Cary, NC). The GC conditions for the THM analysis are summarized in Table 3.3. An extra calibration standard was placed after every ten samples to monitor the calibration curve for drift. From the retention times of the calibration standards, the peak areas of the four THM species were integrated. A relative peak area was defined as the ratio of the peak areas of the calibration standards and samples to the peak area of the internal standard. The relative peak areas were used to correct for any injection volume variations. From the relative peak areas, the individual THM species concentrations for each sample were calculated. All samples were extracted in duplicate and each extract was analyzed. The average of the duplicates was reported. The acceptance criterion dictated that duplicates must be within ±20% of their average.

Table 3.3 Gas chromatographic parameters for analysis of THMs

Parameter	Values
Column	
Type	DB-1 column (Supelco, Bellefonte, PA)
Length	30 m
Internal Diameter	0.25 mm
Film Thickness	1.0 mm
Temperature Sequence:	10 min at 35°C, increase to 150°C at 10°C/min, increase to 250°C at 25°C/min and hold for 11 min: Total Run Time = 36.5 min
Injector	
Injector Volume	2 mL
Temperature	150°C
Detector	
Type	Electron capture
Temperature	300°C
Gases	
Carrier Gas	Helium (Holox, Morrisville, NC)
Carrier Flow	1.2 mL/min at 35°C
Makeup Gas	Nitrogen (Holox, Morrisville, NC)

Since each THM analysis consisted of a raw water and three treated waters, a raw water sample and duplicate were spiked with two to three times the anticipated chloroform concentration (termed matrix spike and matrix spike duplicate). The matrix spikes were used to evaluate the efficiency of the extraction procedure. Under most circumstances, spike recoveries in the range of 80-120% were attained. When spike recoveries were not within the 80-120% range, further analysis revealed it was because the matrix spike concentrations were approximately equal to the sample concentration. Therefore, small changes in the matrix spike concentration resulted in large changes in the spike recovery. When the matrix spike concentration was approximately twice the sample concentration, spike recoveries in the range of 80-120% were attained. The matrix spike recovery along with the extra calibration standards were used as quality control measures. The minimum reporting level (MRL) for all THM4 species was 1 μg/L. When the concentration of individual THM species was less than 1 μg/L, one-half of the MRL (i.e. 0.5 μg/L) was used for calculations.

3.4.9 HAA Analysis

The samples generated by chlorination under UFC were analyzed for HAA9. Analysis was done by micro liquid-liquid extraction, diazomethane derivitization, and gas chromatography with electron capture detection direct injection analysis (Brophy et al. 2000). The standard operating procedure followed was a modification of procedures published by the USEPA (EPA Method 552 1995) and Standard Method 6251B (Standard Methods 1998).

Stock standards of haloacetic acid mix 552 (HAA6: BrAA, BrClAA, ClAA, Br_2AA, Cl_2AA, and Cl_3AA) consisting of 2,000 µg/L of each species in MtBE, and the individual standards $BrCl_2AA$, Br_2ClAA, and Br_3AA at 1,000 µg/L in MtBE were purchased from Supelco (Bellefonte, PA). An acid surrogate (AS) stock standard (2,3-dibromopropionic acid) at 1 mg/L in MtBE was also purchased from Supelco (Bellefonte, PA). The stock standards were received in 1 mL sealed amber glass ampules and, once opened, they were immediately transferred to 5 mL amber vials with screw caps and PTFE-lined silicone septa. PTFE tape was wrapped around the neck of the vials and they were stored in the laboratory standards freezer at -15°C. Certificates of Analysis of all stock standards were kept on file. Stock standards were not used for more than six months after opening of the sealed ampules.

An HAA9 primary calibration standard was prepared by injecting 50 µL of HAA6 and 100 µL of Br_2ClAA, $BrCl_2AA$, and Br_3AA into 5 mL of MtBE (Sigma Aldrich Chemical, Milwaukee, WI). The volumetric flask was filled to the line with MtBE, stoppered, inverted three times, and transferred to a 5 mL amber glass vial with screw cap and PTFE-lined silicone septa. The neck of the vial was wrapped with PTFE tape and stored at -15°C. The HAA9 primary calibration standard was used for up to three months.

IS-1° and IS-2° were prepared as outlined above. An AS additive standard was prepared by injecting 100 µL of the AS stock standard into 5 mL of MtBE (Sigma Aldrich Chemical, Milwaukee, WI). The volumetric flask was filled to the line with MtBE, stoppered, inverted three times, and transferred to a 5 mL amber glass vial with

screw cap and PTFE-lined silicone septa. The neck of the vial was wrapped with PTFE tape and stored at -15°C.

Two reagents were prepared for diazomethane generation. Reagent 1 was prepared by combining 3.3 g diazald (Sigma Aldrich, Milwaukee, WI), 5 mL carbitol (Sigma Aldrich, Milwaukee, WI), and 5 mL of MtBE (Sigma Aldrich, Milwaukee, WI). The vial was gently swirled and capped loosely with a screw cap and PTFE-lined silicone septa. The vial was vented as needed to prevent any pressure build-up. All chemicals used in preparing reagent 1 were put away before the chemicals needed for reagent 2 were placed in the hood. Reagent 2 was prepared by combining 6 mL of DOFW, 10 mL of Burdick & Jackson (Muskegon, MI) high purity methanol for THM analysis, and 4 mL of 45% potassium hydroxide (KOH) (Fisher Scientific, Fair Lawn, NJ). Ten milliliters of MtBE (Sigma Aldrich, Milwaukee, WI) was transferred to a clear 40 mL glass vial to be used as a collection solvent.

The diazomethane generation apparatus consisted of two clear 40 mL glass vials connected by 1.6 mm PTFE tubing and a vent in one of the septa. The cap with the septum vent was screwed onto the 40 mL vial containing the collection solvent. The 1.6 mm PTFE tubing was immersed into the MtBE collection solvent because the diazomethane vapor was collected in the MtBE. The collection solvent vial was then placed in a 500 mL beaker with ice.

Six milliliters of reagent 1 was then transferred to a fourth 40 mL glass vial followed by 6 mL of reagent 2. The vial was immediately capped with the cap and septum connected to the other end of the PTFE tubing. The PTFE tubing was inserted 5-7 cm through the septum so it would collect only vapors and no liquid. Diazomethane vapor then traveled through the PTFE tubing and collected in the MtBE. This reaction lasted 2-3 minutes, until the MtBE collection solvent turned dark yellow. Once the diazomethane generation process was complete, the MtBE/diazomethane solution was capped with a screw cap and PTFE-lined silicone septa, inserted into a double-walled *bomb*, and stored in an explosion-proof freezer. All glassware used in the diazomethane generation process was soaked overnight in a 5N NaOH bath to quench any unreacted diazomethane.

On the day of analysis, the 40 mL sample vials were removed from the refrigerator and allowed to reach room temperature. While the samples were equilibrating to room temperature, six calibration standards were prepared from the HAA9 primary calibration standard. The calibration standards were prepared by injecting the HAA9 standard into DOFW in 100 mL volumetric flasks. Using a 25 mL glass graduated cylinder, a 20 mL aliquot of sample was measured out from the 40 mL sample vials and 100 mL calibration standard volumetric flasks. The samples were poured down the side of the graduated cylinder to reduce air interactions. Between calibration standards and samples, the graduated cylinder was rinsed three times with DOFW and once with 5-10 mL of sample to minimize contamination.

Twenty microliters of AS additive standard was transferred to each 20 mL aliquot of sample/calibration standard using a micro-pipetter. The samples and calibration standards were then acidified by pipetting 1.5 mL of concentrated sulfuric acid (Fisher Scientific, Fair Lawn, NJ) using a pump pipette dispenser. The vials were immediately placed in an ice bath to cool.

An MtBE/IS-2° solution was prepared as outlined above. Four milliliters of MtBE/IS-2° was pipetted into each 20 mL aliquot using a pump pipette dispenser. Approximately 10 g of pre-baked Na_2SO_4 was added to each vial. After addition of the salt, the sample vial was Vortex-mixed (Type 16700 Mixer-MaxiMix I, Thermolyne, Dubuque, IA) for one minute. The samples were then allowed to settle for five minutes to allow any undissolved salt crystals to settle to the bottom and to allow the two liquids to separate.

A 9 in. disposable glass Pasteur pipette was used to transfer 2 mL of the MtBE layer to a 2 mL volumetric flask. A clean pipette was used for each sample. Approximately ½ of a small, rounded scoop of anhydrous, powdered magnesium sulfate ($MgSO_4$) (Sigma Aldrich, Milwaukee, WI) was added to each 2 mL of MtBE extract. The magnesium sulfate was used as a drying agent to minimize the effects of water on the derivatization process (Brophy et al. 2000). Two hundred microliters of cold diazomethane was added on top of the MtBE. The derivatization process converted the polar haloacetic acids to their corresponding haloesters since the haloesters are chromatographable. The 2 mL volumetrics were capped and stored in a refrigerator for

15 minutes. The samples were taken out of the refrigerator and allowed to equilibrate to room temperature for 15 minutes, after which they were inspected for a faint yellow color indicating that enough diazomethane was present to drive the esterification process to completion. Any samples not having a faint yellow color were noted in the lab notebook. Finally, a small rounded scoop of silicic acid n-hydrate ($SiO_2 \cdot nH_2O$) (J.T. Baker, Phillipsburg, NJ) was added to each sample to quench any residual diazomethane.

A 9 in. glass Pasteur pipette was employed to transfer approximately 1 mL of MtBE solution to a clear glass autosampler vial capped with an aluminum-PTFE faced seal (Laboratory Supply Distributors Corp., Mt. Laurel, NJ). The extracts were stored at -15°C until analyzed. Derivatized sample extracts and calibration standard extracts were analyzed on a Hewlett-Packard model 5890A GC with an ECD (Hewlett-Packard Co., Cary, NC). The GC conditions for the HAA analysis are summarized in Table 3.4. A procedure identical to that used for THM analysis was used to quantify HAA species concentrations in the samples. Extra calibration standards and matrix spikes were analyzed in an analogous fashion to the THM analysis as quality control measures. Under most circumstances, spike recoveries in the range of 70-130% were attained. When spike recoveries were not within the 70-130% range, further analysis revealed it was because the matrix spike concentrations were approximately equal to the sample concentration. Therefore, small changes in the matrix spike concentration resulted in large changes in the spike recovery. When the matrix spike concentration was approximately twice the sample concentration, spike recoveries in the range of 70-130% were attained. The acceptance criterion for duplicates was ±20%. The minimum reporting level for all HAA9 species was 2 μg/L. When the concentration of individual HAA species was less than 2 μg/L, one-half of the minimum reporting level (i.e. 1 μg/L) was used for calculations

Table 3.4 Gas chromatographic parameters for analysis of HAAs

	Parameter	Values
Column		
	Type	DB-1 column (Supelco, Bellefonte, PA)
	Length	30 m
	Internal Diameter	0.25 mm
	Film Thickness	1.0 mm
	Temperature Sequence:	
	21 min at 37°C, increase to 136°C at 5°C/min and hold for 3 min, increase to 250°C at 20°C/min and hold for 3 min: Total Run Time = 52.5 min	
Injector		
	Injector Volume	2 mL
	Temperature	180°C
Detector		
	Type	Electron capture
	Temperature	300°C
Gases		
	Carrier Gas	Helium (Holox, Morrisville, NC)
	Carrier Flow	1.2 mL/min at 37°C
	Makeup Gas	Nitrogen (Holox, Morrisville, NC)

CHAPTER 4

RESULTS AND DISCUSSION

4.1 RAW WATER CHARACTERISTICS

The raw water characteristics of the four waters examined in this study are summarized in Table 4.1. All waters have a slightly alkaline pH. The waters are characterized by relatively low turbidity, low to moderate organic carbon concentrations, a wide range of alkalinities, and moderate to high bromide concentrations. The DOC accounts for greater than 90% of the corresponding TOC for all the waters. SUVA is the ratio of UV254 to DOC, and tends to be strongly correlated with the aromatic carbon content of NOM in a water (Croue et al. 1999). NBA water has the highest SUVA (3.8 L $mg^{-1}m^{-1}$) while SL water has the lowest SUVA (2.0 L $mg^{-1}m^{-1}$). Based on these SUVA values, NBA water is expected to be dominated by hydrophobic organic substances while SL water is expected to have a sizable hydrophilic fraction. This has implications for water treatment because raw waters with high SUVA values are more amenable to TOC removal by coagulation than low SUVA waters (White et al. 1997, Liang and Singer 2003) and tend to have a higher DBP formation potential (Reckhow et al. 1990, Croue et al. 1999, Liang and Singer 2003).

NBA water and SL water had the highest THM4 formation potentials (THM4FPs) because they also had the highest DOC concentrations among the four waters examined. NBA water had the highest HAA9 formation potential (HAA9FP) because it had the highest concentration of UV-absorbing substances and the highest SUVA. This is consistent with the findings of Liang and Singer (2003) who demonstrated that waters with high SUVA values had higher concentrations of hydrophobic organic carbon, and had a greater tendency to produce HAAs than waters with lower SUVA values that were dominated by hydrophilic organic carbon.

Waters with a high alkalinity or a high bromide concentration or both tend to have a high concentration of total dissolved solids (TDS). Such waters would be expected to have a high concentration of anionic species that might compete with NOM for exchange

sites on the MIEX resin, thereby impacting NOM removal by ion exchange. The moderate to high bromide concentration is also expected to result in substantial incorporation of bromine into the THMs and HAAs upon chlorination of these waters.

Table 4.1 Raw water characteristics

Raw water	pH	Turbidity	Alkalinity	Bromide	UV254	TOC	DOC	SUVA	THM4FP	HAA9FP
		NTU	mg/L as $CaCO_3$	µg/L	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$	µg/L	µg/L
NBA	7.5	20	149	76	0.193	5.5	5.1	3.8	294	224
CL	8.6	7	92	240	0.074	2.3	2.5	3.0	150	65.3
SBA	7.8	6	57	83	0.064	1.9	1.9	3.4	111	90.5
SL	8.1	6	188	540	0.102	5.2	5.1	2.0	283	127

4.2 PRELIMINARY JAR-TEST RESULTS

Preliminary jar-test experiments were conducted to determine appropriate coagulant and MIEX doses. Appendix B contains the results of all preliminary jar-test experiments.

Figure 4.1 illustrates the impact of MIEX dose and mixing time on the removal of UV-absorbing material from SBA water. For a given mixing time, as the MIEX dose increases, UV absorbance decreases. For all MIEX doses, UV absorbance plateaus at about 20 minutes. UV absorbance was also observed to plateau at about 20 minutes for the other three waters examined. These results are consistent with Singer and Bilyk (2002) who observed that the majority of UV254 removal by treatment with MIEX occurred in the first 20-30 minutes.

Figure 4.2 displays the affect of MIEX dose on the removal of UV-absorbing organics and DOC. Both UV absorbance and the concentration of DOC decrease as the MIEX dose increases. The curves show that UV absorbance and DOC tend to track each other. Similar results were found for the other three waters. This suggests that MIEX removes a wide range of dissolved organic materials, and does not solely remove UV-absorbing organic matter.

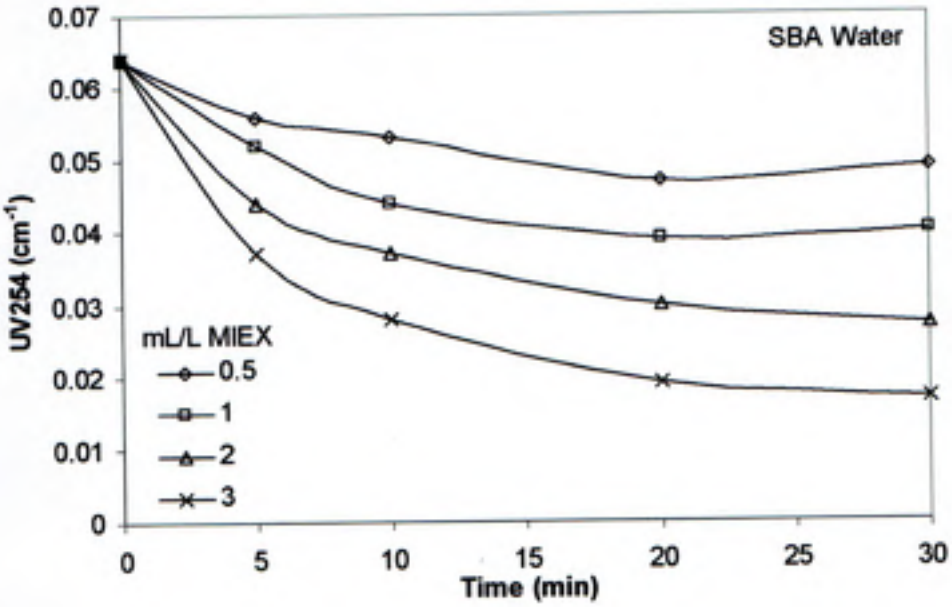

Figure 4.1 Illustrative impact of MIEX dose and mixing time on UV absorbance at 254 nm

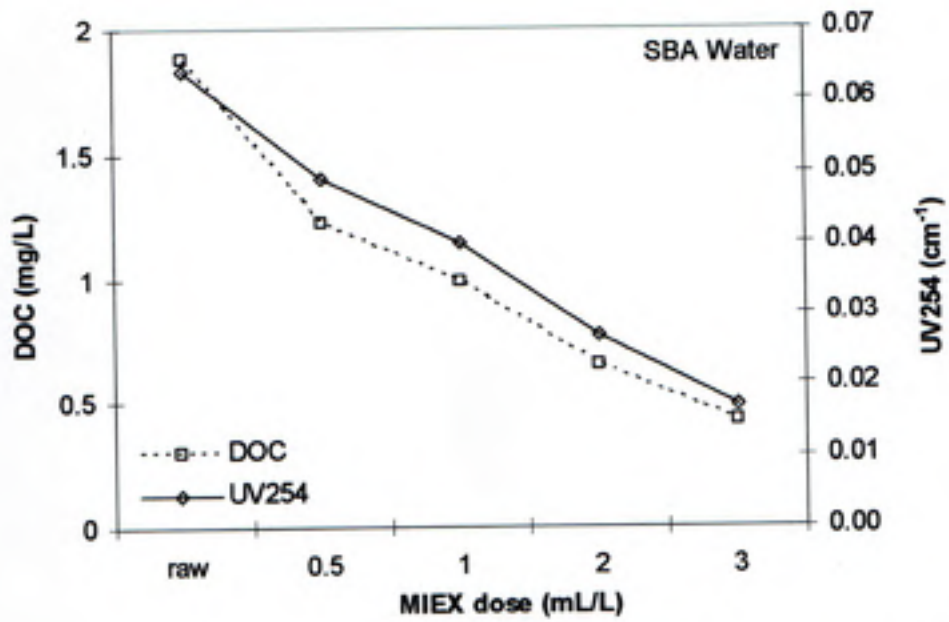

Figure 4.2 Illustrative impact of MIEX dose on DOC and UV absorbance at 254 nm

4.3 COAGULATION, TREATMENT WITH MIEX, AND TREATMENT WITH MIEX PLUS COAGULATION

Using results from the preliminary jar-tests as guidance, appropriate doses of alum and MIEX were chosen to generate large volumes of treated water for THM and HAA analysis and for NOM fractionation (see Table 4.2). Note that the doses tend to be consistent with the UV absorbance and DOC content of the raw waters in that higher doses are required as the DOC concentration and UV absorbance of the raw water increase. Appendix C contains detailed water quality data for the raw waters and the treated waters.

Table 4.2 Coagulant and MIEX doses selected for treatment of each water

Water	Alum (mg/L)	MIEX (mL/L)	MIEX (mL/L) + Alum (mg/L)
NBA	60	5	5 + 16
CL	20	2	2 + 4
SBA	10	2	2 + 5
SL	40	4	4 + 20

4.3.1 Impact on UV Absorbance

Figure 4.3 displays the UV absorbance at 254 nm for the raw water and the three treated waters for each location. For all locations, treatment with MIEX reduced the UV absorbance more than coagulation. There does not appear to be a substantial difference in UV absorbance after MIEX treatment compared to MIEX treatment plus coagulation.

Figure 4.4 illustrates the impact of coagulation, treatment with MIEX, and treatment with MIEX plus coagulation on the removal of UV absorbance. Coagulation removed 15-40% of the UV absorbance while treatment with MIEX and treatment with MIEX followed by coagulation removed 50-80% of the UV absorbance. Figure 4.4 shows that the percent removal of UV absorbance is directly related to the SUVA of the raw water for all three treatment practices. This suggests that coagulation and ion exchange (i.e. MIEX) are more effective at removing UV absorbance in waters with a high SUVA (i.e. greater than 3.0 L $mg^{-1}m^{-1}$) and less effective in waters with a low

SUVA (i.e. less than 3.0 L $mg^{-1}m^{-1}$). In addition to having the lowest SUVA, SL water has a high anionic composition, so this could partially explain why treatment with MIEX was less effective in this water.

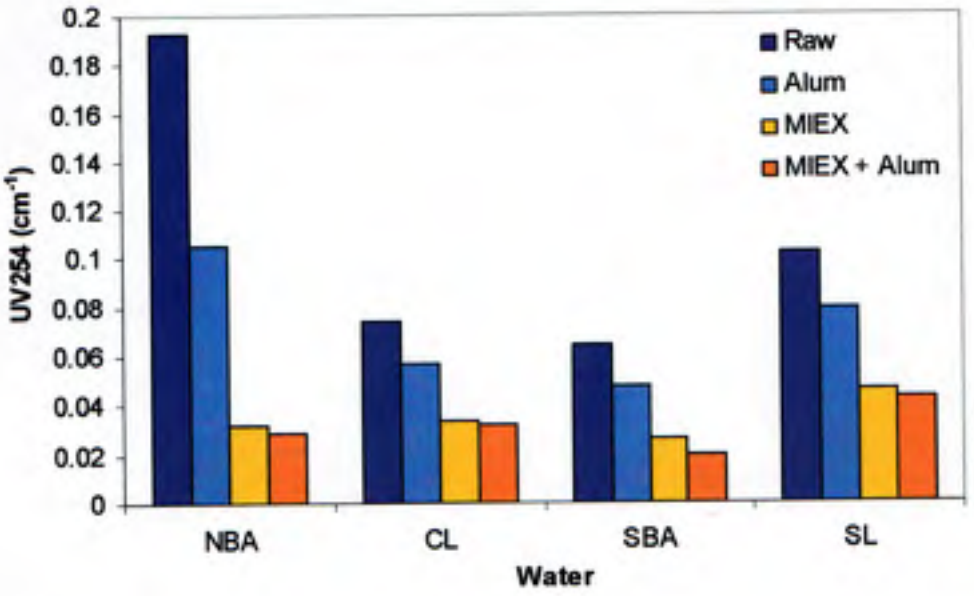

Figure 4.3 UV absorbance at 254 nm before and after treatment for each location

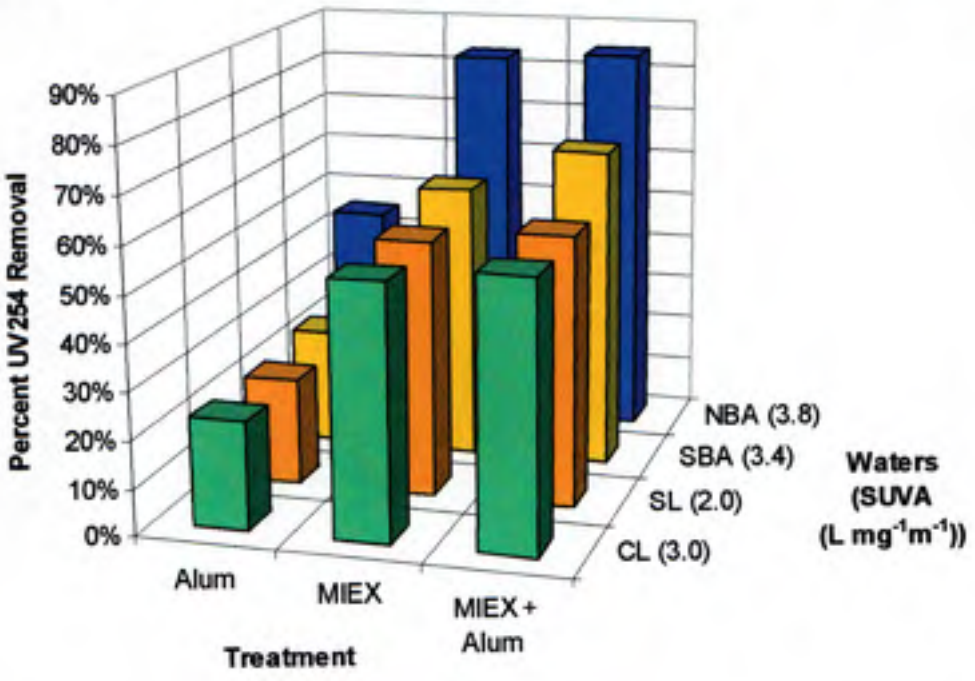

Figure 4.4 Impact of treatment on percent removal of UV absorbance at 254 nm for each location

4.3.2 Impact on DOC

Figure 4.5 displays the DOC concentrations of the raw water and the three treated waters for each location. The results are similar to those for UV absorbance. As the initial DOC concentration of the raw water decreases, the effectiveness of all three treatment practices for removal of DOC decreases. For all locations, treatment with MIEX reduced the DOC concentration of the raw water to a greater extent than coagulation. Treatment with MIEX and treatment with MIEX plus coagulation reduced the concentration of DOC to a similar extent.

Figure 4.6 illustrates the impact of coagulation, treatment with MIEX, and treatment with MIEX followed by coagulation on the percent removal of DOC. Coagulation removed 10-30% of the DOC, whereas treatment with MIEX removed 30-75% of the DOC. The effectiveness of coagulation and ion exchange for removal of DOC decreases with decreasing SUVA, but is also dependent on the initial DOC concentration of the raw water. Raw waters characterized by low concentrations of DOC and low SUVA values gave lower DOC removals. CL water and SL water both had high anion concentrations, so this could also explain the decrease in DOC removal by ion exchange for these waters.

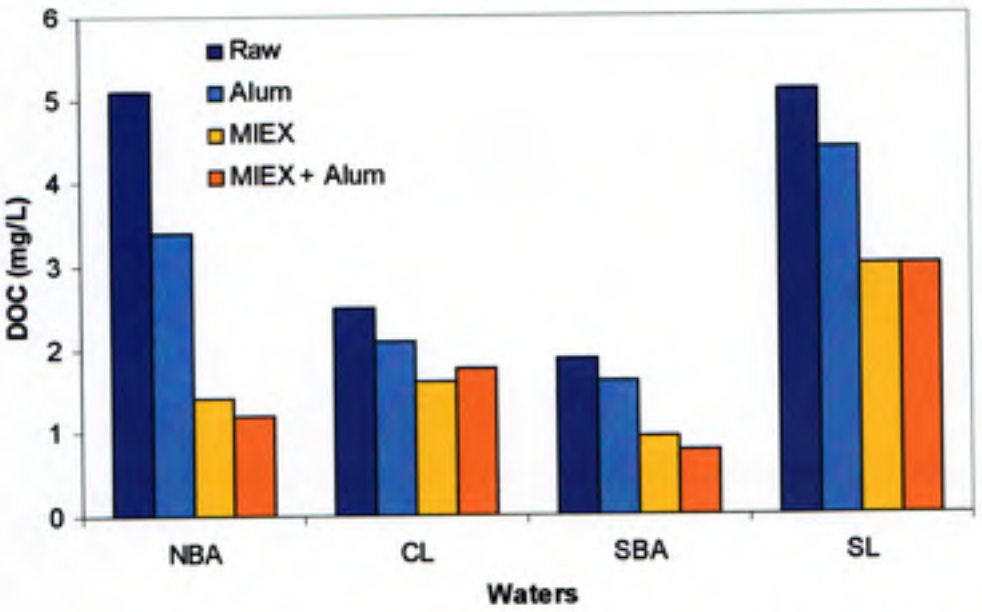

Figure 4.5 DOC concentrations of water before and after treatment for each location

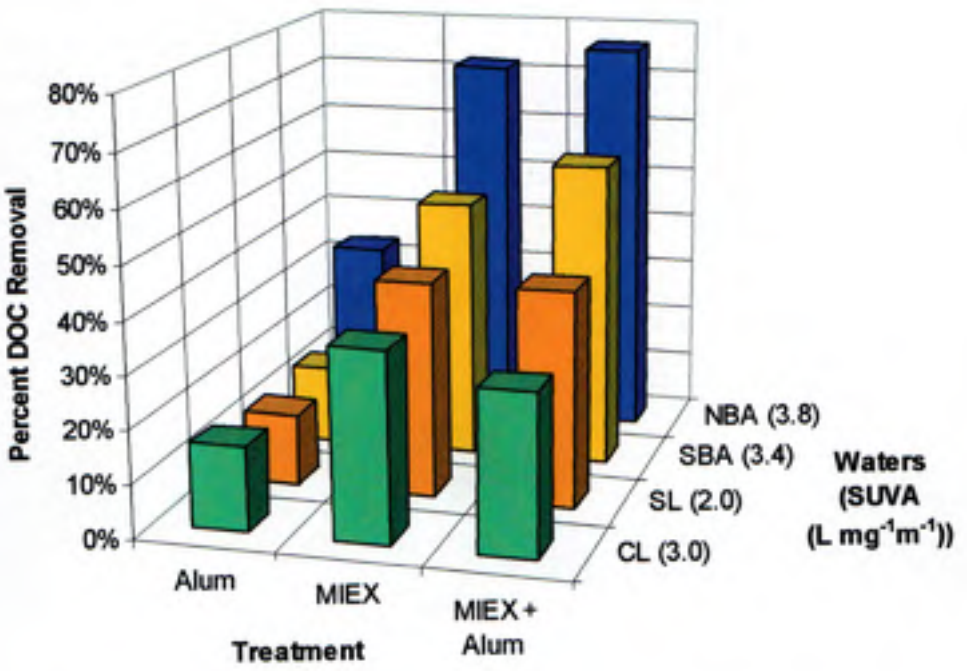

Figure 4.6 Impact of treatment on percent removal of DOC for each location

4.3.3 Impact on Bromide

Table 4.3 presents the bromide concentrations of the raw waters and treated waters for each location. As expected, coagulation did not remove bromide to any appreciable extent for any of the waters. Treatment with MIEX removed bromide to varying degrees. This was expected because Singer and Bilyk (2002) observed that the MIEX resin was capable of removing bromide, although the extent of removal depended on the alkalinity (i.e. carbonate content) of the water. For SBA water, the water with the lowest carbonate content, treatment with MIEX reduced the raw water bromide concentration by about 45%. For SL water and CL water, the waters with the highest bromide concentrations, treatment with MIEX reduced the raw water bromide concentration only by about 15%. Bromide removal by MIEX was most effective in waters with a low alkalinity and a relatively low raw water bromide concentration. Similar trends were also observed by Johnson and Singer (2003), suggesting that in waters with a high anionic composition, species such as carbonate, bicarbonate, chloride, and sulfate may compete with bromide and NOM for exchange sites on the MIEX resin.

Table 4.3 Effect of treatment on bromide removal

Water Source	Treatment	Bromide (µg/L)
NBA	Raw	76
NBA	60 mg/L Alum	73
NBA	5 mL/L MIEX	55
NBA	5 mL/L MIEX + 16 mg/L Alum	56
CL	Raw	240
CL	20 mg/L Alum	240
CL	2 mL/LMIEX	200
CL	2 mL/L MIEX + 4 mg/L Alum	190
SBA	Raw	83
SBA	10 mg/L Alum	85
SBA	2 mL/LMIEX	46
SBA	2 mL/L MIEX + 5 mg/L Alum	43
SL	Raw	540
SL	40 mg/L Alum	530
SL	4 mL/L MIEX	460
SL	4 mL/L MIEX + 20 mg/L Alum	470

4.3.4 Impact on THM4 AND HAA9 Formation Potential

All water analyzed for THMs and HAAs were chlorinated under UFC (see §3.3.5). The THM4FP and the HAA9FP are defined as μg/L of DBPs formed under UFC. Figures 4.7-10 display the THM4FP and the HAA9FP for all four raw and treated waters. The error bars on the bar graphs indicate the measured formation potentials for duplicate DBP samples from a single chlorinated sample. For all the waters, the HAA9FP was less than the THM4FP. This was expected since the waters were chlorinated at pH 8, and researchers have shown that THM concentrations increase with increasing pH while X_3AA concentrations and overall HAA9 concentrations decrease with increasing pH (Pourmoghaddas et al. 1993, Liang and Singer 2003).

Alum coagulation was most effective in NBA water for reducing both THM4FP and HAA9FP (see Figure 4.7). This was expected since the characteristics of NBA raw water (i.e. high SUVA) suggest it would be readily amenable to TOC removal and the removal of UV-absorbing organics by coagulation. Figures 4.8 and 4.10 illustrate that coagulation did not reduce the THM4FP or HAA9FP for CL water and SL water, respectively, to any significant degree. Both CL and SL raw water had high alkalinities and low SUVA values. These results are consistent with the findings of Krasner and Amy (1995) and White et al. (1997) that SUVA determines the effectiveness of coagulation for removal of DBP precursors.

Treatment with MIEX reduced the THM4FP and HAA9FP in all waters. Treatment with MIEX was more effective at reducing the THM4FP and HAA9FP than coagulation for all four waters. Treatment with MIEX had the greatest impact on THM4FP and HAA9FP reduction in NBA water (see Figure 4.7), and was least effective at reducing THM4FP and HAA9FP in SL water (see Figure 4.10). NBA water had a high SUVA, whereas SL water had a lower SUVA and a high concentration of competing anionic species. This suggests that MIEX treatment will remove more DBP precursors in waters with high SUVA values or low anionic composition or both. Treatment with MIEX followed by coagulation did not seem to improve removal of THM4FP and HAA9FP over treatment with MIEX alone. This implies that treatment with MIEX removes a wide range of organic materials, including the fraction readily removed by

coagulation. This is supported by observations that the removal of UV-absorbing substances by MIEX tended to track the removal of overall DOC (see Figure 4.2).

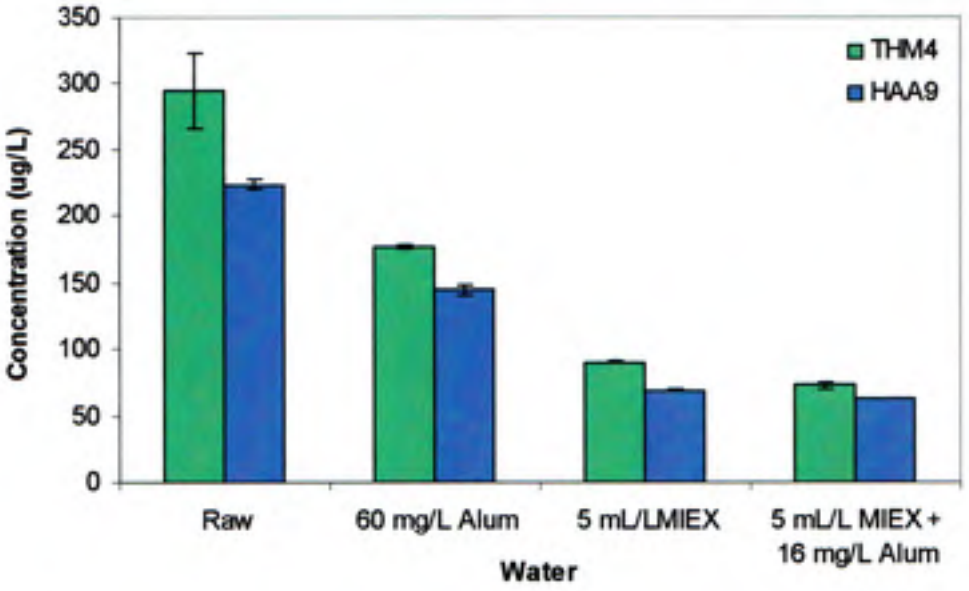

Figure 4.7 THM4 and HAA9 formation potential before and after treatment for NBA water (raw water SUVA 3.8 L $mg^{-1}m^{-1}$)

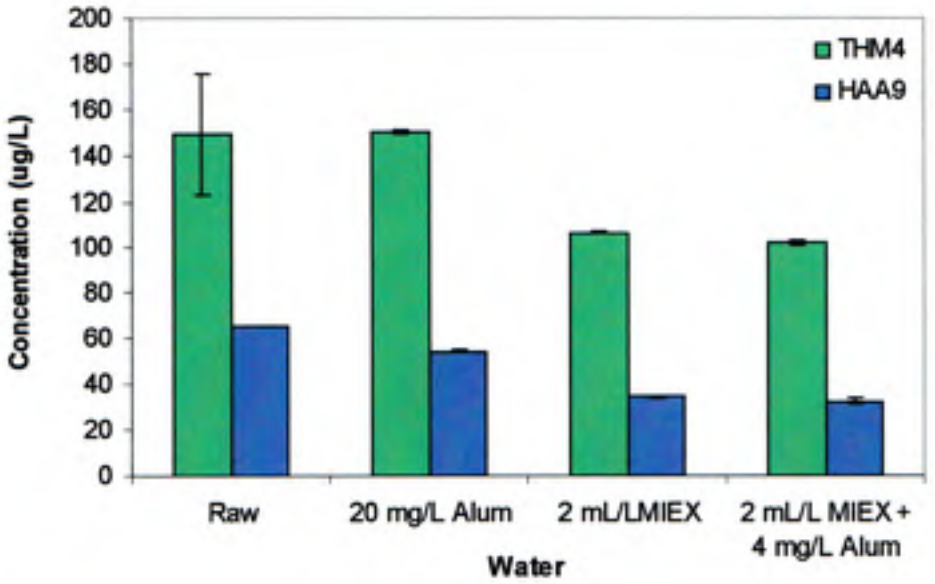

Figure 4.8 THM4 and HAA9 formation potential before and after treatment for CL water (raw water SUVA 3.0 L $mg^{-1}m^{-1}$)

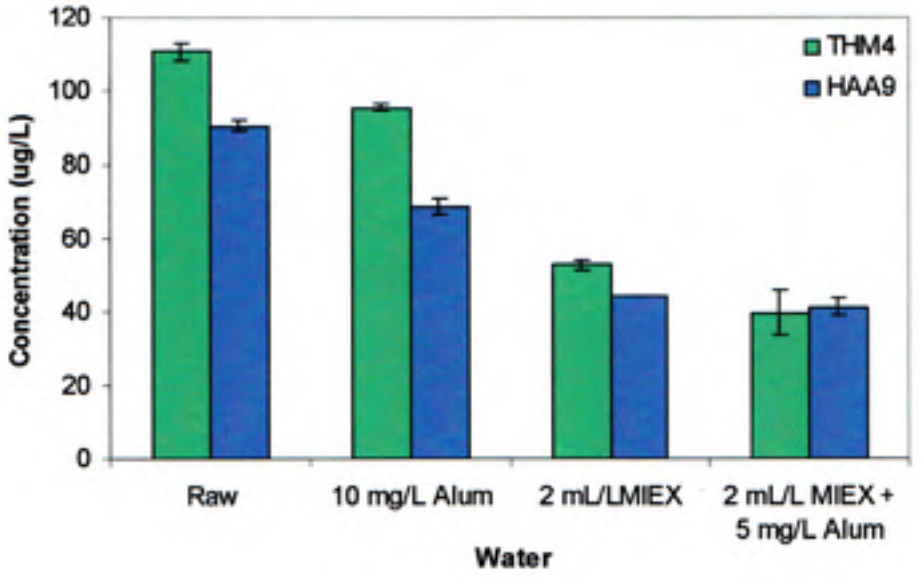

Figure 4.9 THM4 and HAA9 formation potential before and after treatment for SBA water (raw water SUVA 3.4 L $mg^{-1}m^{-1}$)

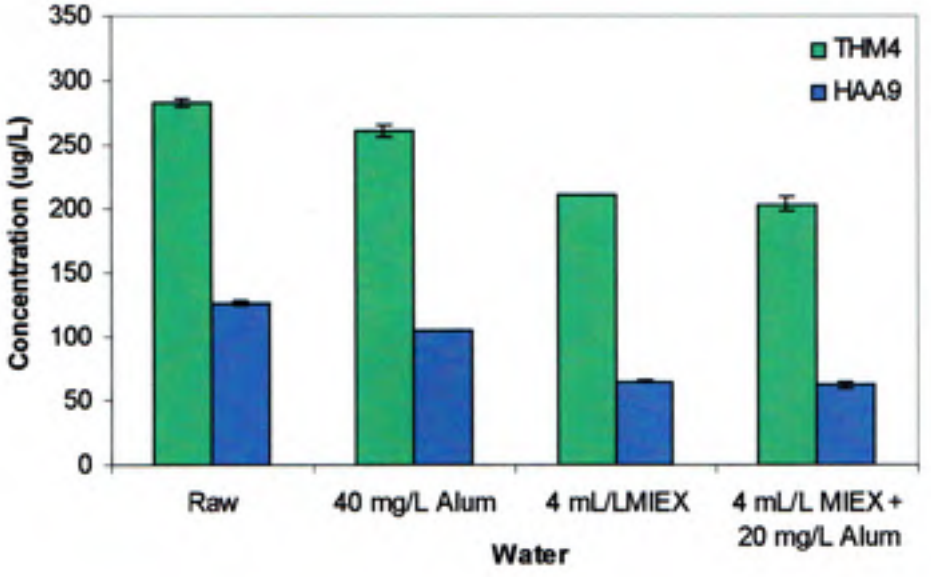

Figure 4.10 THM4 and HAA9 formation potential before and after treatment for SL water (raw water SUVA 2.0 L $mg^{-1}m^{-1}$)

Figures 4.11 and 4.12 summarize the impact of treatment on removal of THM4FP and HAA9FP, respectively, for all four waters. In Figure 4.11, coagulation shows no removal of THM4FP for CL water and removal of THM4FP in the range of 5-40% for the other waters. Treatment with MIEX had a low THM4FP removal of 20% for SL water and a high THM4FP removal of 70% for NBA water. Treatment with MIEX and treatment with MIEX followed by coagulation display a similar degree of THM4FP removal. For all treatments, removal of THM4FP tended to increase as the SUVA of the raw water increased.

Figure 4.12 illustrates the impact of treatment on the removal of HAA9FP and shows similar trends to Figure 4.11. Coagulation reduced HAA9FP 10-40%, while treatment with MIEX removed approximately 50% of HAA9FP for CL, SBA, and SL waters and 70% of HAA9FP for NBA water. Treatment with MIEX and treatment with MIEX followed by coagulation show similar HAA9FP removals. Comparing Figures 4.11 and 4.12, for the raw waters with higher SUVA values (i.e. NBA water and SBA water), the percent removal of THM4FP and HAA9FP by treatment with MIEX are similar (e.g. treatment with MIEX removed approximately 70% of the THM4FP and 70% of the HAA9FP for NBA water). In contrast, for the raw waters with lower SUVA values (i.e. CL water and SL water), the percent removal of HAA9FP was greater than the percent removal of THM4FP (e.g. treatment with MIEX removed 50% of the HAA9FP but only 20% of the THM4FP for SL water). This suggests that treatment with MIEX preferentially removes HAA precursors in waters with a low humic content.

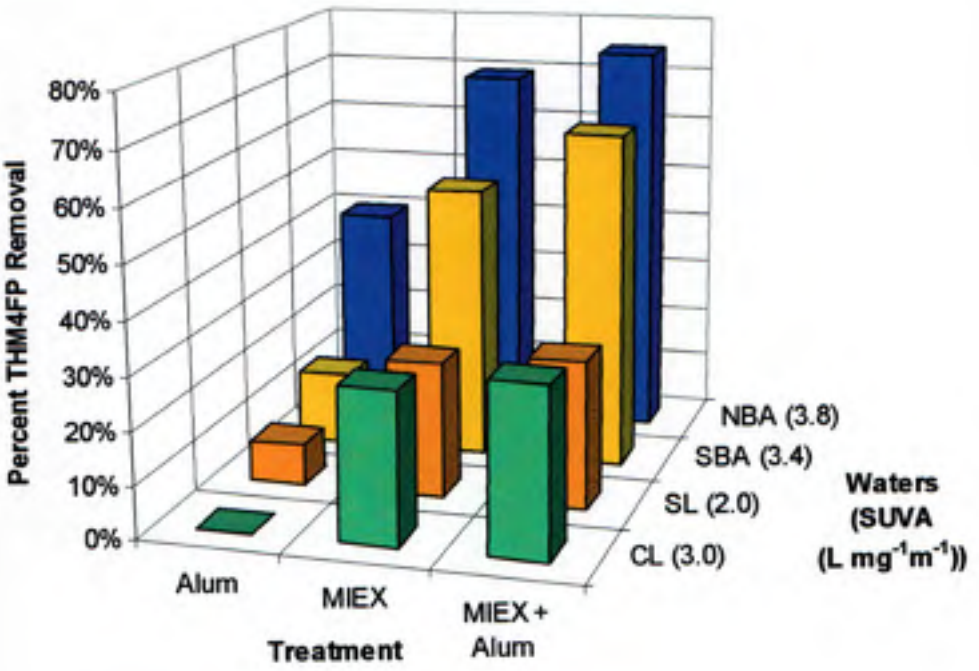

Figure 4.11 Impact of treatment on removal of THM4 formation potential

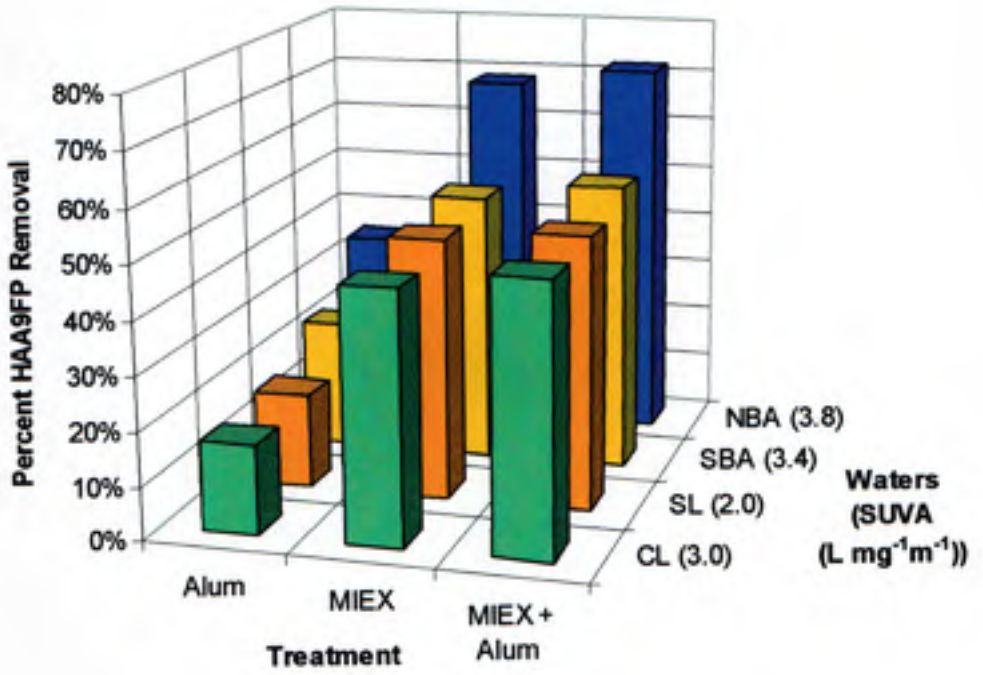

Figure 4.12 Impact of treatment on removal of HAA9 formation potential

4.4 THM and HAA Speciation

Researchers have shown that as the concentration of bromide in the raw water increases, the speciation of THMs and HAAs shifts toward the more brominated species (Pourmoghaddas et al. 1993, Cowman and Singer 1996, McLain et al. 2002). Many treatment practices for DBP control focus on removing NOM. As a result, the ratio of Br/TOC increases causing more bromine to be incorporated into the DBP species.

4.4.1 Impact of Br/TOC and Br/Cl_2 on THM4 and HAA9 Speciation for Raw Waters

Figure 4.13 illustrates the impact of the Br/TOC ratio and the Br/Cl_2 ratio on the speciation of THMs for the four raw waters. For the Br/Cl_2 ratio, Cl_2 represents the concentration of chlorine that was consumed during chlorination (i.e. chlorine dose minus chlorine residual). The concentration of the individual THM species is expressed as a mole fraction to account for the differences in molecular weights of the species. The insert within Figure 4.13 shows that the Br/TOC and Br/Cl_2 ratios are directly proportional to each other and, as both of these ratios increase, the speciation of THMs shifts toward the more brominated species. NBA raw water has the lowest Br/TOC and Br/Cl_2 ratios and, as a result, chloroform accounts for approximately 90% of THM4 on a molar basis. In contrast, CL raw water and SL raw water have the highest Br/TOC and Br/Cl_2 ratios and, correspondingly, SL raw water has a more uniform distribution of THM species with chloroform accounting for only 20% of THM4 on a molar basis and bromoform accounting for greater than 10%.

Based on these results, one would expect similar patterns for HAA9 speciation. This is verified by Figure 4.14 which displays the impact of the Br/TOC ratio and the Br/Cl_2 ratio on the speciation of HAAs following chlorination of the four raw waters. Analogous to the results in Figure 4.13 the speciation of HAAs shifts to the more brominated species as the ratios of Br/TOC and Br/Cl_2 increase. This is seen for both the dihaloacetic acid and trihaloacetic acid classes of the HAAs. Figure 4.14 illustrates similar trends to those observed by Cowman and Singer (1996), with dichloroacetic acid

and trichloroacetic acid being the dominant species in water with low bromide concentrations and the bromine-containing di- and trihaloacetic acids being dominant in waters with a high bromide concentration. For NBA raw water, dichloroacetic acid and trichloroacetic acid account for approximately 80% of HAA9 on a molar basis, whereas for SL raw water, these same two species account for only 20% of HAA9. In SL water, the mixed chloro-bromo and fully brominated species are the dominant HAA species.

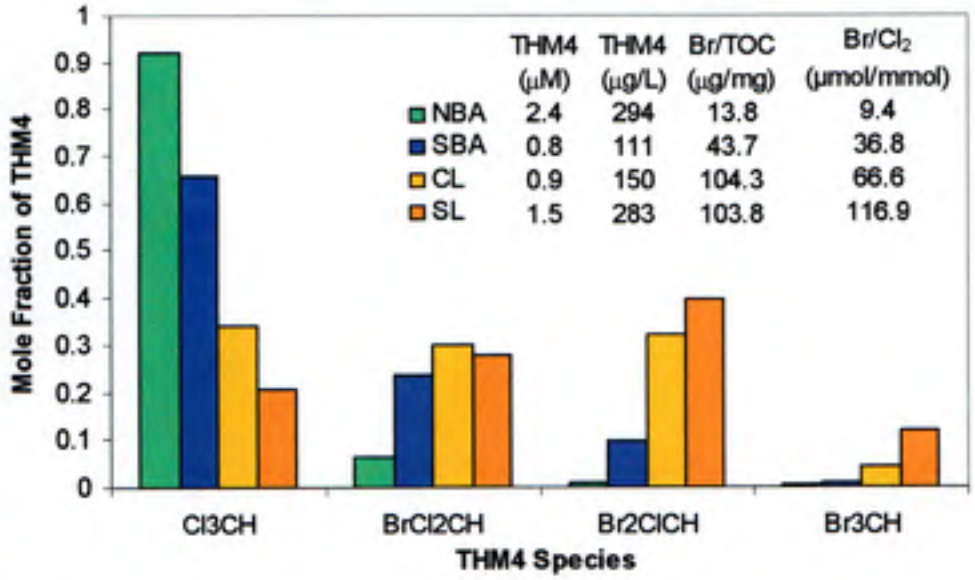

Figure 4.13 Impact of Br/TOC and Br/Cl_2 ratios on THM4 speciation in the four raw waters

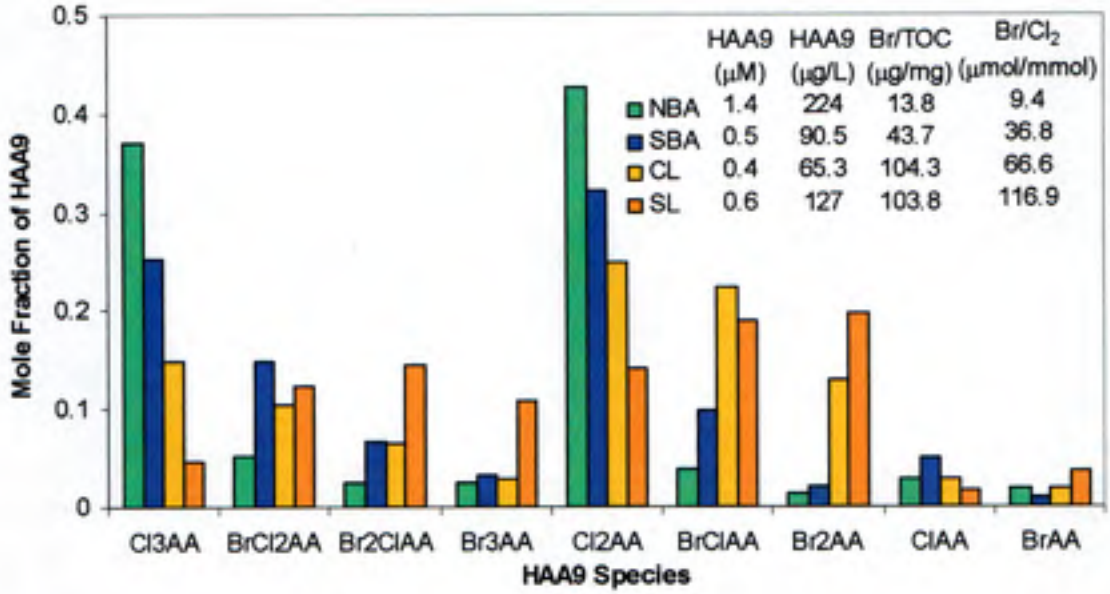

Figure 4.14 Impact of Br/TOC and Br/Cl_2 ratios on HAA9 speciation in the four raw waters

4.4.2 Impact of Coagulation and Treatment with MIEX on THM4 Speciation

Section 4.4.1 illustrated the shift in THM and HAA speciation toward the more brominated species as the Br/TOC ratio of the raw water increased. Because NOM is removed to a greater extent than bromide by most DBP precursor removal processes, one would also expect the Br/TOC ratio to increase after treatment, causing a shift toward the more brominated species following chlorination. Summers et al. (1993) noted an increase in the Br/TOC ratio after activated carbon adsorption, anion exchange, and membrane filtration treatment, and observed a corresponding shift to the more brominated THMs following chlorination of the treated water compared to chlorination of the raw water. Figure 4.15 and Figure 4.16 show the impact of coagulation and treatment with MIEX on the speciation of THM4 for NBA water and SL water, respectively. NBA and SL waters are shown because they have comparable concentrations of DOC and the greatest difference in bromide concentrations. Similar figures for CL water and SBA water are presented in Appendix D.

For NBA water, Figure 4.15 illustrates the decrease in the mole fraction of chloroform with respect to NBA raw water following coagulation and treatment with MIEX and the corresponding increase in the mole fractions of bromodichloromethane and dibromochloromethane. For the raw water, the mole fractions of chloroform and bromodichloromethane were 0.93 and 0.07, respectively. Following treatment with MIEX, the mole fraction of chloroform decreased to 0.71 while the mole fraction of bromodichloromethane increased to 0.25. A similar pattern is observed after coagulation. Figure 4.16 shows similar trends for coagulation and treatment with MIEX for SL water.

In general, treatment reduces the mole fraction of the more chlorinated species with respect to the raw water and increases the mole fraction of the more brominated species. Because treatment with MIEX was shown to reduce the concentration of DOC to a greater extent than coagulation, it is expected that the Br/TOC ratio following treatment with MIEX would be greater than after coagulation, resulting in greater reductions in the mole fractions of the more chlorinated THM species and correspondingly greater increases in the mole fractions of the more brominated THM species. This is verified in Figure 4.15 and Figure 4.16

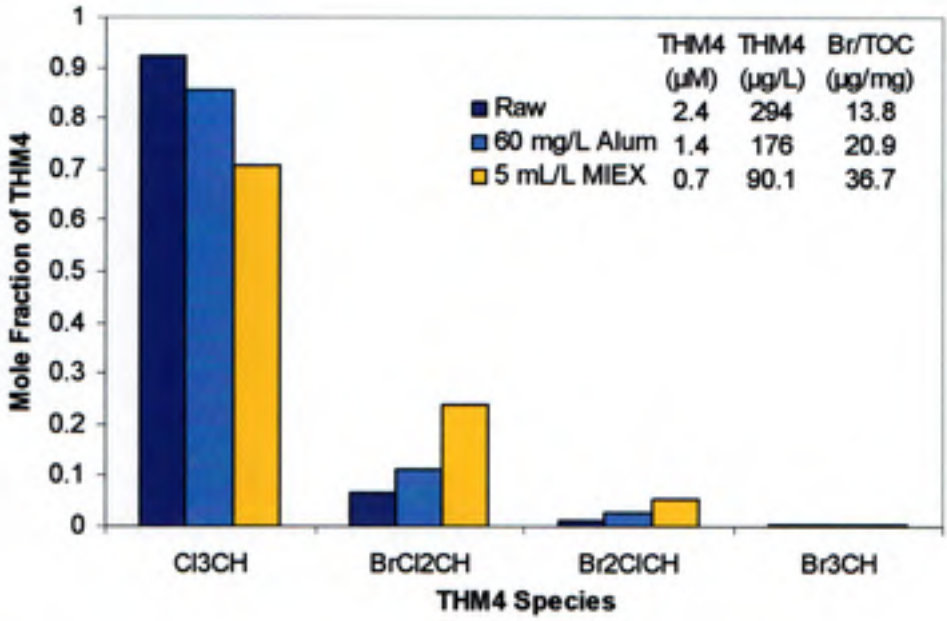

Figure 4.15 Impact of coagulation and treatment with MIEX on THM4 speciation for NBA water

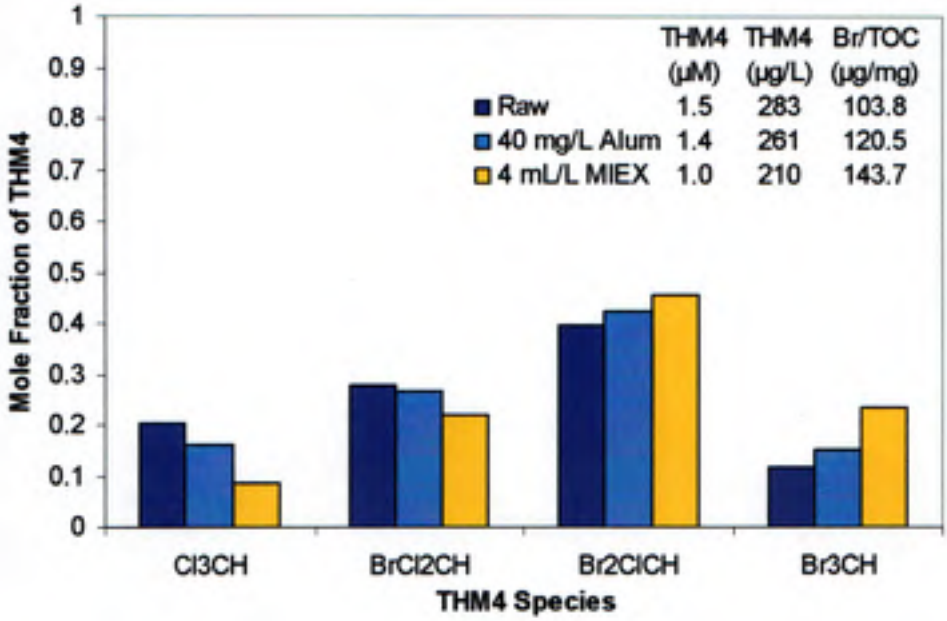

Figure 4.16 Impact of coagulation and treatment with MIEX on THM4 speciation for SL water

4.4.3 Impact of Coagulation and Treatment with MIEX on HAA9 Speciation

Because coagulation and treatment with MIEX cause a shift to the more brominated THM species, it is expected that a shift to the more brominated HAA species would also be observed. This is illustrated in Figure 4.17 and Figure 4.18 for NBA water and SL water, respectively. Figure 4.17, which shows HAA9 speciation for NBA water, illustrates very similar trends to those seen in Figure 4.15 for THM4 speciation for NBA water. Both coagulation and treatment with MIEX reduce the mole fractions of dichloroacetic acid and trichloroacetic acid while the mole fractions of the bromine-containing di- and trihaloacetic acids increase. Figure 4.18, for SL water, displays similar trends as Figure 4.16 for THM4 speciation of SL water and as Figure 4.17 for HAA9 speciation of NBA water, with treatment reducing the mole fraction of the more chlorinated HAA species and increasing the mole fraction of the more brominated species. Both Figure 4.17 and Figure 4.18 show that, because treatment with MIEX removes more NOM than coagulation and results in a greater increase in the Br/TOC ratio, there is a greater decrease in the mole fractions of the more chlorinated HAA9 species and a greater increase in the mole fractions of the more brominated HAA9 species after MIEX treatment compared to coagulation.

The results of Sections 4.4.2 and 4.4.3 indicate that treatment with MIEX is effective at limiting the formation of chlorinated DBPs but that the mole fraction of some of the brominated DBPs in the treated water will be greater than in the raw water. Depending on the reduction of overall THM4FP and HAA9FP in the treated water relative to the raw water, it is possible that the concentration of some brominated THM and HAA species may be higher in the chlorinated treated water following treatment with alum and/or MIEX than in the chlorinated raw water.

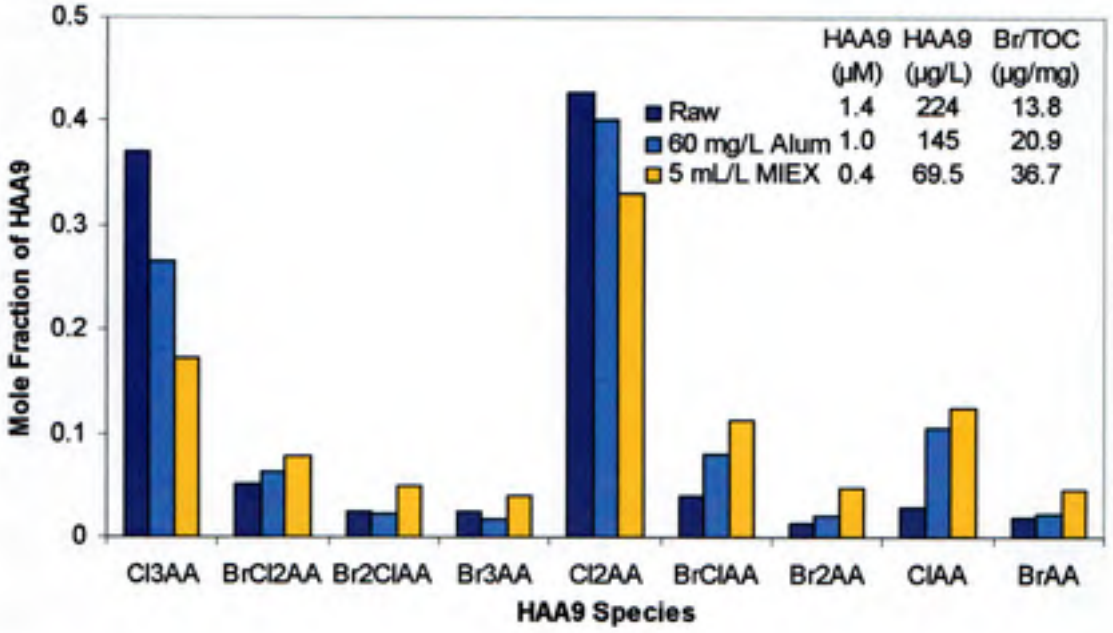

Figure 4.17 Impact of coagulation and treatment with MIEX on HAA9 speciation for NBA water

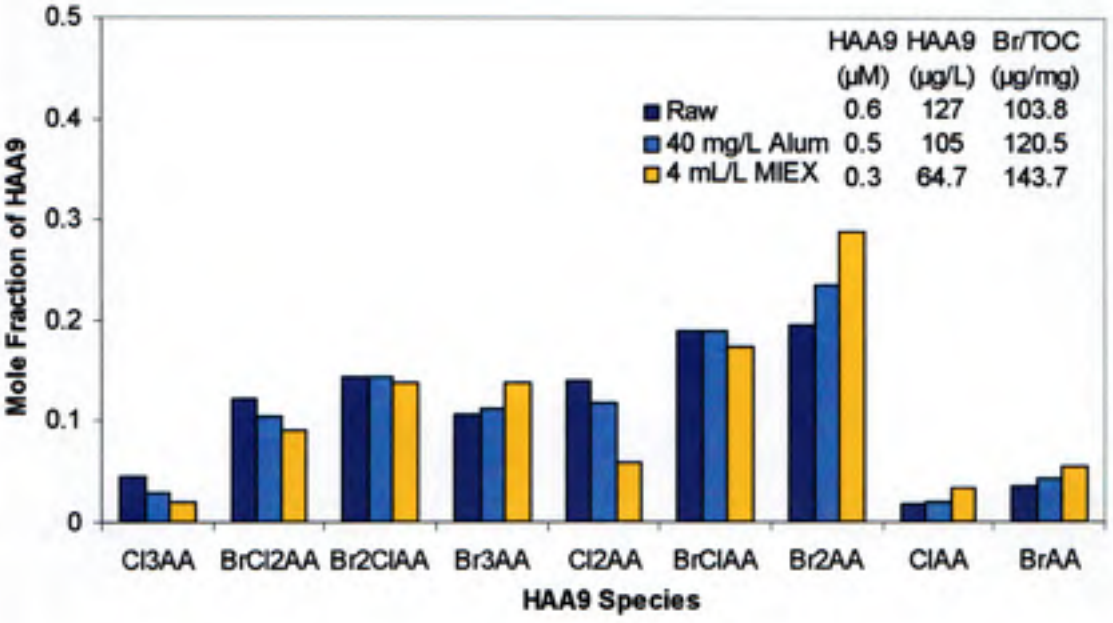

Figure 4.18 Impact of coagulation and treatment with MIEX on HAA9 speciation for SL water

4.4.4 Bromine Incorporation

In Chapter 2, the bromine incorporation factor was defined as the ratio of moles of bromine to moles of total halogen incorporated into the various classes of DBP species. This normalizes the bromine incorporation factor to a value between zero and one for each class of DBPs. For example, for THM4, a bromine incorporation factor of zero means chloroform is the only THM species while a bromine incorporation factor of one means bromoform is the only THM species. Figures 4.19, 4.20, and 4.21 show comparisons of the bromine incorporation factors among THM4, X_2AA, and X_3AA DBP classes. The solid line corresponds to the theoretical 1:1 line (i.e. $y = x$) if bromine incorporation was the same for both DBP classes shown. Markers falling near the 1:1 line indicate that bromine incorporation into the class shown on the y-axis is approximately equal to bromine incorporation into the class shown on the x-axis. Figure 4.19 shows the bromine incorporation factor for the three X_2AA species compared to the four THM species. Figure 4.19 suggests that bromine incorporation into X_2AAs mirrors bromine incorporation into THM4. Similar observations were noted by Obolensky and Singer (2003) based on an analysis of the ICR database.

Figure 4.20 shows the corresponding bromine incorporation factor for the four X_3AA species compared to the four THM species. The relationship of bromine substitution into X_3AAs and THM4 conform reasonably well to the 1:1 line. Obolensky and Singer (2003) observed that bromine substitution into X_3AAs was approximately 20% lower than for THM4.

Figure 4.21 shows the bromine incorporation factor for X_3AAs compared to X_2AAs. This figure suggests that bromine substitution into the four X_3AAs tends to track bromine substitution into the three X_2AAs. This seems to be a reasonable result since similar trends between X_2AA and X_3AA species were observed for the results presented and discussed in the previous sections.

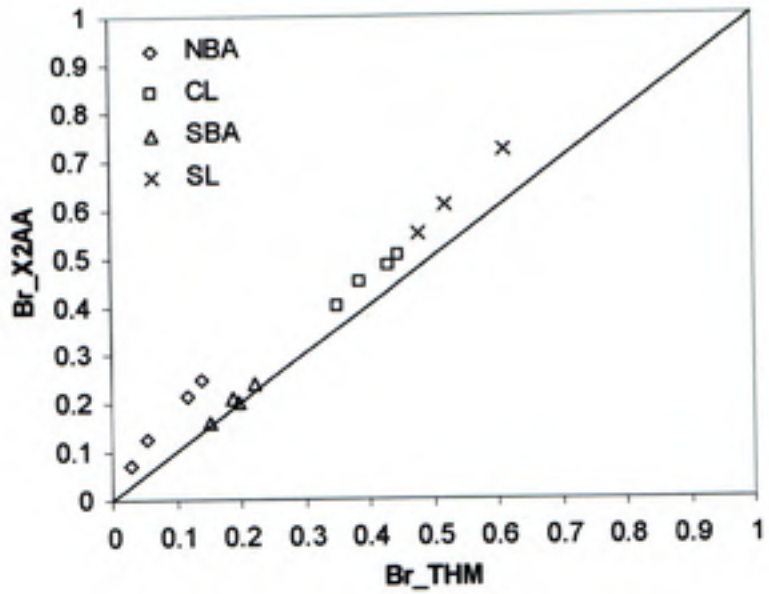

Figure 4.19 Comparison of bromine incorporation into dihaloacetic acids and trihalomethanes

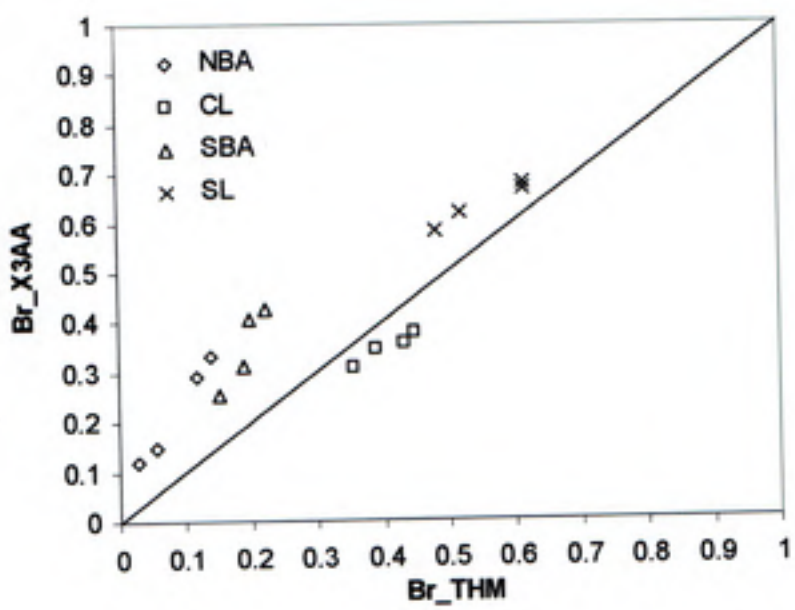

Figure 4.20 Comparison of bromine incorporation into trihaloacetic acids and trihalomethanes

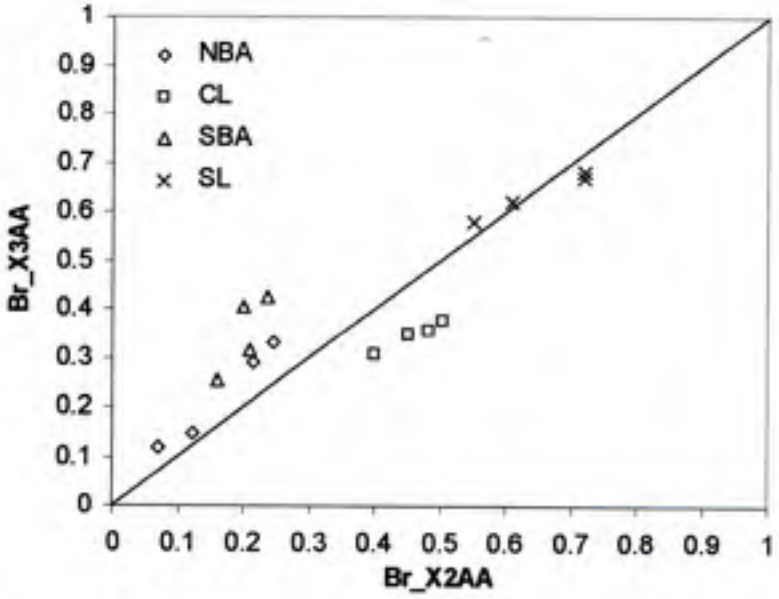

Figure 4.21 Comparison of bromine incorporation into trihaloacetic acids and dihaloacetic acids

4.5 XAD FRACTIONATION

Raw water and treated waters were separated into HPOA, TPHA, and HPIA fractions using the XAD-8/XAD-4 resin fractionation technique (Thurman and Malcolm 1981, Leenheer 1981, Aiken et al. 1992). Figures 4.22-26 illustrate the results of XAD fractionation experiments for NBA and SL raw and treated waters. Because both NBA raw water and SL raw water had appreciable concentrations of DOC, there is less uncertainty in their fractionation results. Results of fractionation experiments on SBA water and CL water (see Appendix E) are more uncertain due to the relatively low concentration of DOC in the raw water. Fractions flagged with an asterisk (*) indicate that the measured DOC concentration of that fraction is less than the lowest calibration standard (0.5 mg/L), so its DOC value is less certain. Fractions flagged with a dagger (†) indicate that the measured DOC value of the treated water fraction is greater than the corresponding measured raw water fraction. Since treatment removes DOC, the concentration of DOC of the individual fractions can only decrease with respect to the corresponding raw water fractions. Since the precision of the TOC analyzer is ±0.2

mg/L, this most likely accounts for the apparent increase in the DOC value of the treated water fraction. Therefore, fractions flagged with a dagger (†) indicate that its DOC value is less certain.

Figure 4.22 shows the distribution of DOC among the XAD fractions for NBA raw water, coagulated water, and water treated with MIEX. For NBA raw water, the HPOA fraction accounts for 48% of the total DOC while the HPIA fraction accounts for only 21%. This was expected based on the relatively high SUVA of NBA raw water. Following coagulation, the DOC concentration of all three fractions is reduced, but the HPOA and TPHA fractions are reduced to the greatest extent. Treatment with MIEX reduces the DOC concentration of all three organic acid fractions to a similar degree and to a much greater extent than coagulation. These trends are illustrated in Figure 4.23. For the coagulated water, approximately 30% of the DOC associated with the three organic acid fractions was removed. In contrast, treatment with MIEX removed approximately 70% of the DOC associated with the three organic acid fractions.

Figure 4.24 shows the distribution of DOC among the three XAD fractions for SL raw water, coagulated water, and MIEX-treated water. The distribution of HPOA, TPHA, and HPIA fractions in SL water contrasts with that in NBA water, which was expected based on their respective SUVA values. Both the HPOA and HPIA fractions account for approximately 35% of the DOC concentration of SL raw water, with the TPHA fraction accounting for the least DOC. These results are consistent with the literature which indicates that the SUVA of a water is a good indicator of the relative distribution of the humic and non-humic fractions. After coagulation with alum, the concentration of DOC associated with the HPOA and HPIA fractions decreased, whereas the TPHA fraction appears to have slightly increased relative to that of the raw water. The TPHA fractions in both the raw water and coagulated water are most likely approximately equal and the lack of precision of the TOC analyzer accounts for the apparent increase. Figure 4.25 illustrates the impact of coagulation and treatment with MIEX on the removal of organic acid fractions for SL water. Treatment with MIEX decreased the DOC concentration of all three fractions to a greater extent than coagulation. Treatment with MIEX also decreased the DOC concentration of all three fractions by a similar degree with the HPIA fraction being removed to the greatest extent.

Neither coagulation nor treatment with MIEX was as effective at removing the different organic acid fractions in SL water compared to NBA water. For example, removal of DOC associated with the HPOA fraction in SL water by coagulation is 12% compared to 33% for NBA water. Treatment with MIEX removed 38% of the DOC associated with the HPOA fraction for SL water compared to 76% for NBA water.

An additional set of experiments was conducted to define more clearly how the dose of MIEX affected the organic fractions removed. Figure 4.26 shows these results. For any given MIEX dose, the percent removal of DOC of all three organic acid fractions is similar and increases as the MIEX dose increases. These results indicate that treatment with MIEX removes both humic and non-humic substances to a similar extent.

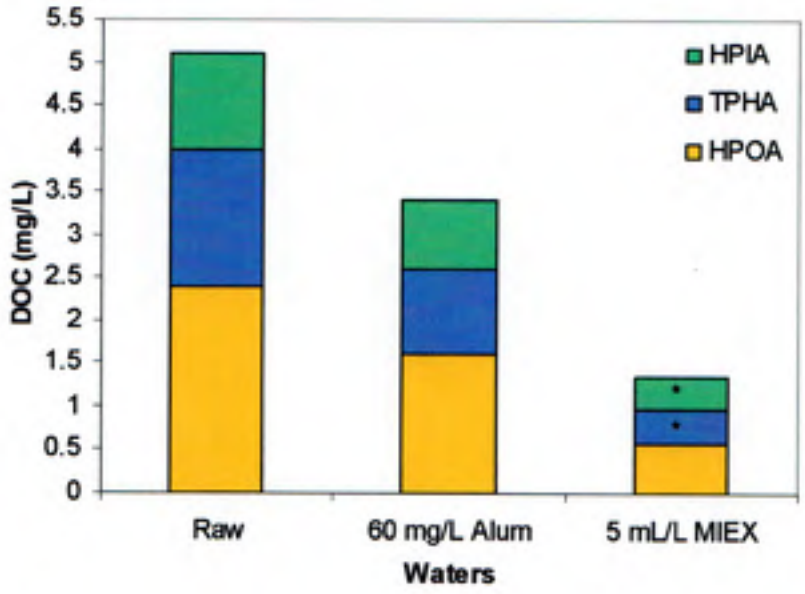

Figure 4.22 Distribution of XAD fractions for raw and treated NBA water (raw water SUVA 3.8 L $mg^{-1}m^{-1}$) (* uncertain; see text)

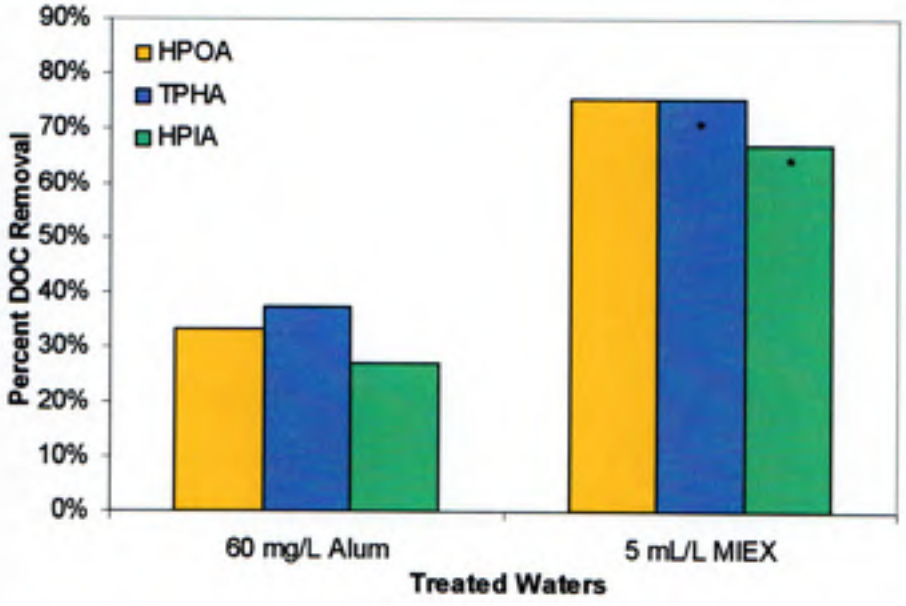

Figure 4.23 Impact of coagulation and treatment with MIEX on the removal of organic acid fractions for NBA water (raw water SUVA 3.8 L $mg^{-1}m^{-1}$) (* uncertain; see text)

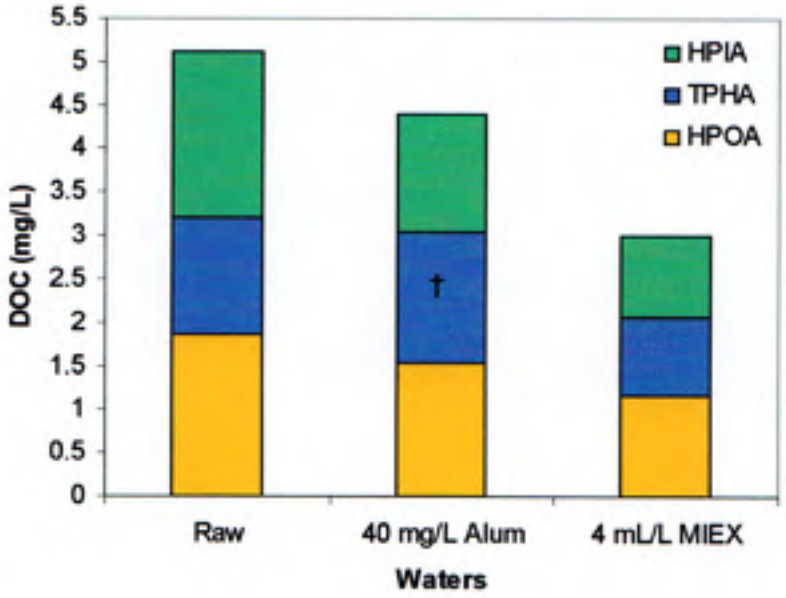

Figure 4.24 Distribution of XAD fractions for raw and treated SL water (raw water SUVA 3.8 L $mg^{-1}m^{-1}$) († uncertain; see text)

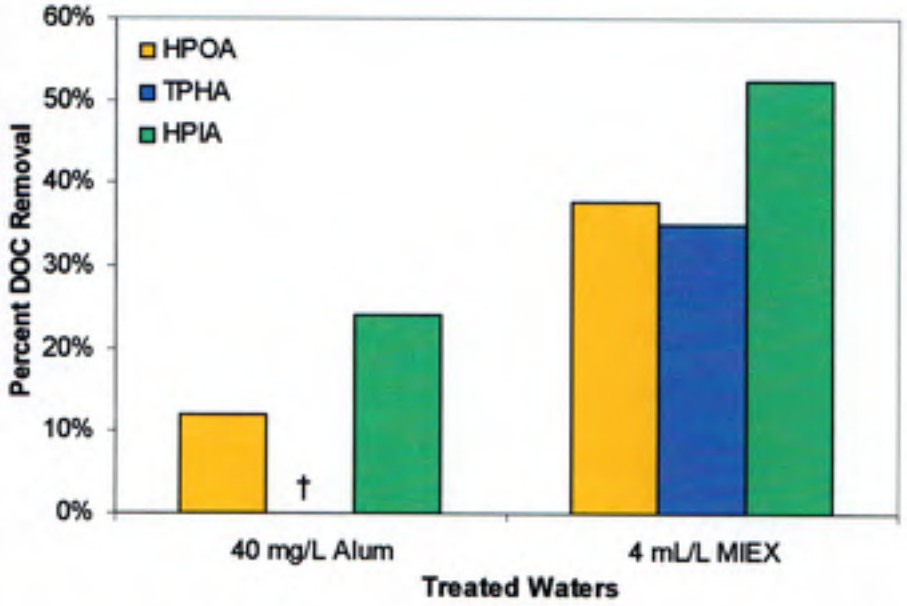

Figure 4.25 Impact of coagulation and treatment with MIEX on the removal of organic acid fractions for SL water (raw water SUVA 2.0 L $mg^{-1}m^{-1}$) († uncertain; see text)

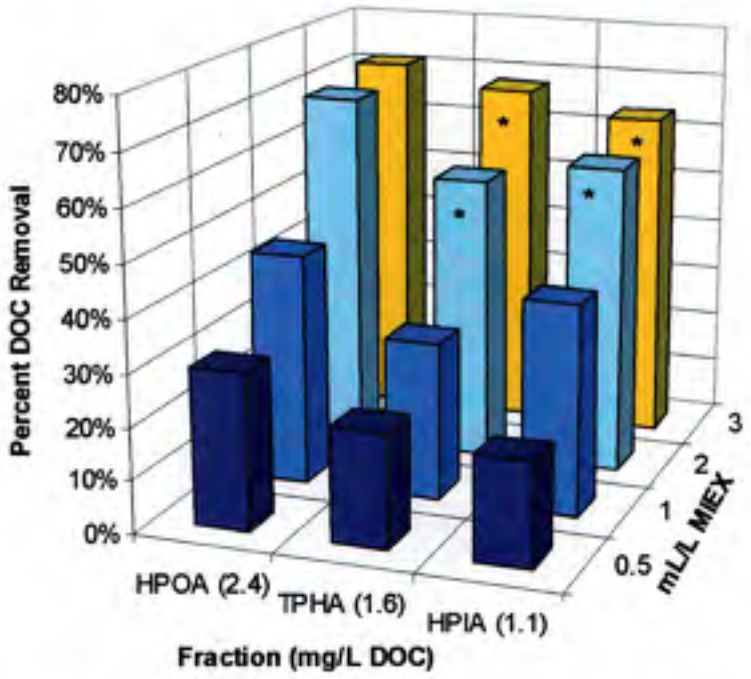

Figure 4.26 Impact of different MIEX doses on the removal of various organic acid fractions for NBA water (* uncertain; see text)

4.6 MOLECULAR WEIGHT FRACTIONATION

The molecular weight distribution of the raw water and treated waters was determined by ultrafiltration. Samples of raw and treated water were filtered, in parallel, through membranes with a 1,000, 10,000, and 30,000 Dalton nominal molecular weight cutoff. This yielded four fractions with AMWs of <1k, 1-10 k, 10-30 k, and >30k. The >30k fraction was the smallest fraction in all of the raw waters and had the greatest analytical uncertainty. Fractions flagged with an asterisk (*) or a dagger (†) are uncertain due to the reasons discussed in § 4.5.

Figure 4.27 displays the AMW fractions for raw and treated NBA water. The difference in the DOC concentration between the raw water and the filtrate from the 30k membrane was approximately zero, so the DOC concentration associated with the >30k fraction was assigned a value of zero. NBA raw water was dominated by DOC in the 1-10k fraction. Coagulation reduced the DOC concentration of the 1-30k fractions but had

little impact on the DOC concentration of the <1k fraction. This is consistent with the literature, where coagulation is noted to preferentially remove larger molecular weight organics. For NBA water, because treatment with MIEX removed significant amounts of the HPOA, TPHA, and HPIA fractions, it was expected that treatment with MIEX would also remove a wide range of AMW fractions of DOC. Figure 4.28 shows that this was indeed the case. Treatment with MIEX effectively removed more of the DOC associated with the 1-30k fractions than coagulation did and also removed the smaller molecular weight organics in the <1k fraction which coagulation did not remove. Figure 4.28 illustrates that coagulation removed 60% of the DOC associated with the 1-10k fraction and lesser amounts for the other fractions. Treatment with MIEX removed approximately 60% of the DOC associated with the <1k fraction and almost 90% of the DOC associated with the 10-30k fraction. These results indicate that in raw waters with a high SUVA, treatment with MIEX will remove a wider range of AMW fractions and greater amounts of each fraction than coagulation.

Figure 4.29 displays the corresponding AMW fractions for raw and treated SL water. SL water was dominated by smaller molecular weight DOC than NBA water. For SL water, 42% of the DOC was associated with the <1k fraction compared to 23% for NBA water. This was expected since SL water had a low SUVA and a large proportion of hydrophilic DOC which suggests that the DOC has a smaller molecular weight. For SL water, the DOC concentration of the >30k AMW fraction was approximately zero. Figure 4.30 illustrates the impact of alum and MIEX treatment on the percent removal of DOC in the different AMW fractions for SL water. Both coagulation and treatment with MIEX removed 50-60% of the DOC associated with the 10-30k fraction. Coagulation was not effective at removing DOC associated with the 1-10k or <1k fractions, whereas DOC removal of the 1-10k fraction by treatment with MIEX was comparable to removal of the 10-30k fraction. Treatment with MIEX was not effective at removing DOC associated with the <1k fraction for this water, in contrast to what was observed for NBA water.

Figures for CL water and SBA water are presented in Appendix F and show similar trends. Results of the molecular weight fractionation experiments indicate that

treatment with MIEX removes more DOC associated with a wider range of AMW fractions (i.e. <1-30k) than coagulation.

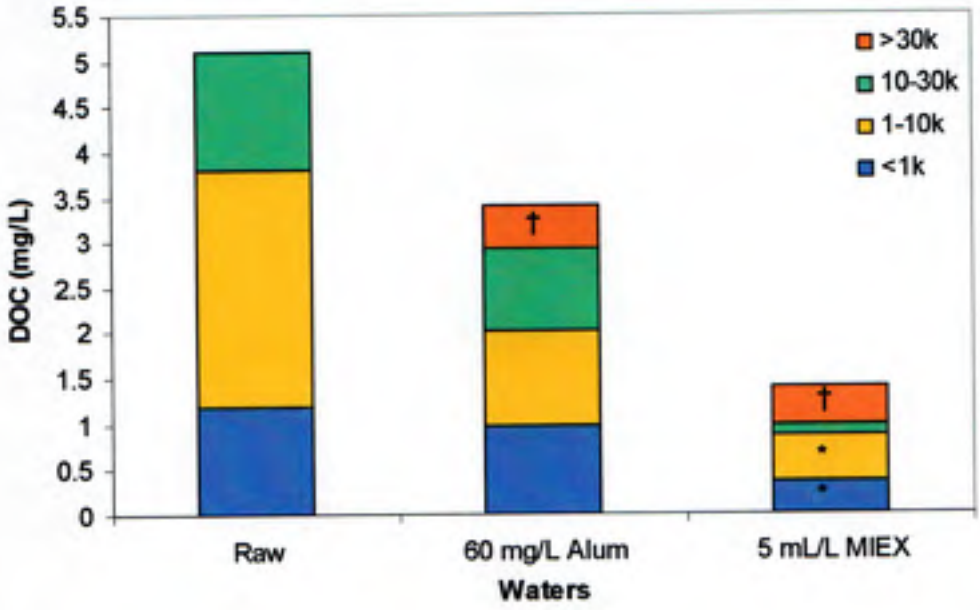

Figure 4.27 Apparent molecular weight fractions of NBA water before and after treatment (raw water SUVA 3.8 L $mg^{-1}m^{-1}$) (*, † uncertain; see text)

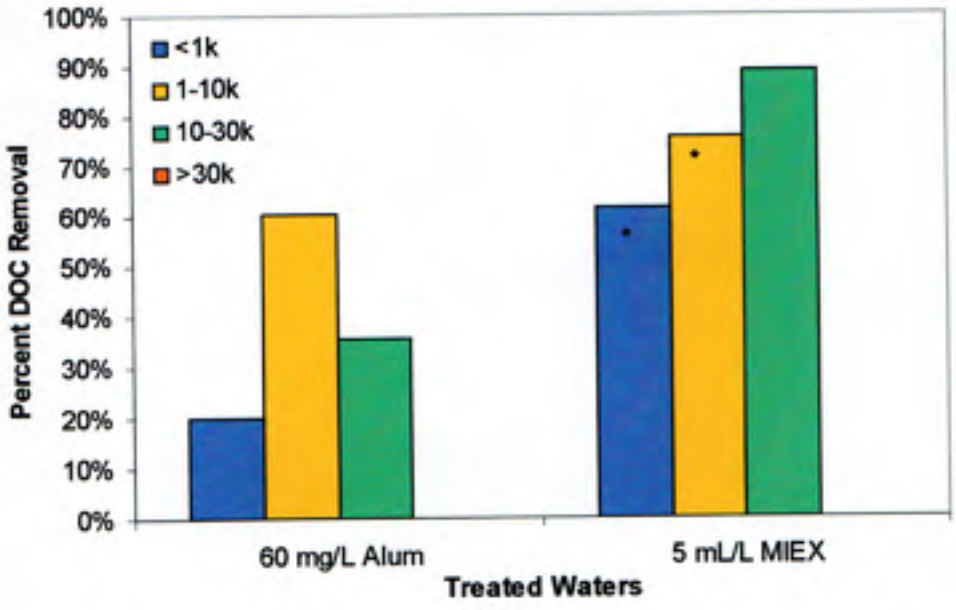

Figure 4.28 Impact of coagulation and treatment with MIEX on the removal of different molecular weight fractions for NBA water (* uncertain; see text)

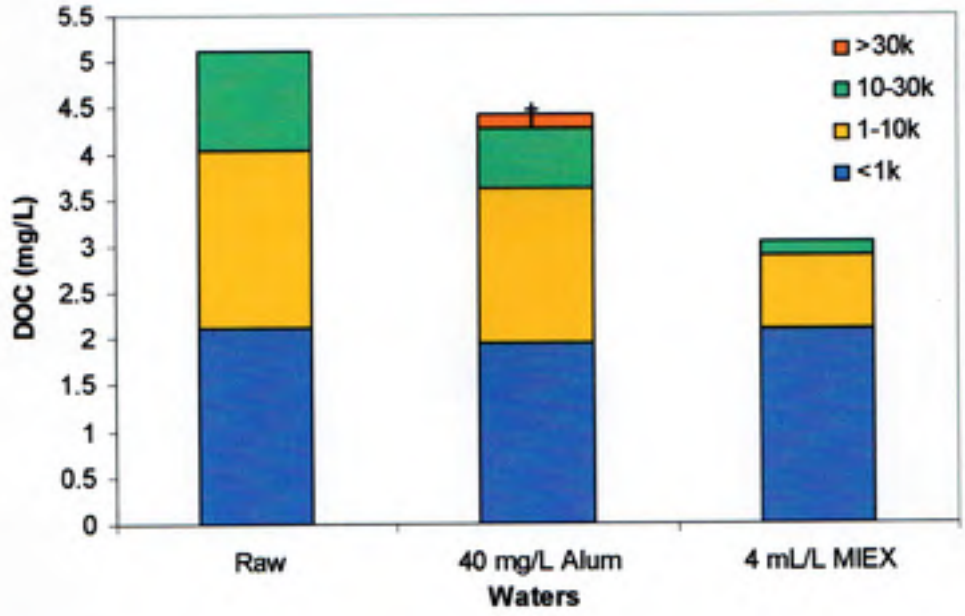

Figure 4.29 Apparent molecular weight fractions of SL water before and after treatment (raw water SUVA 2.0 L $mg^{-1}m^{-1}$) († uncertain; see text)

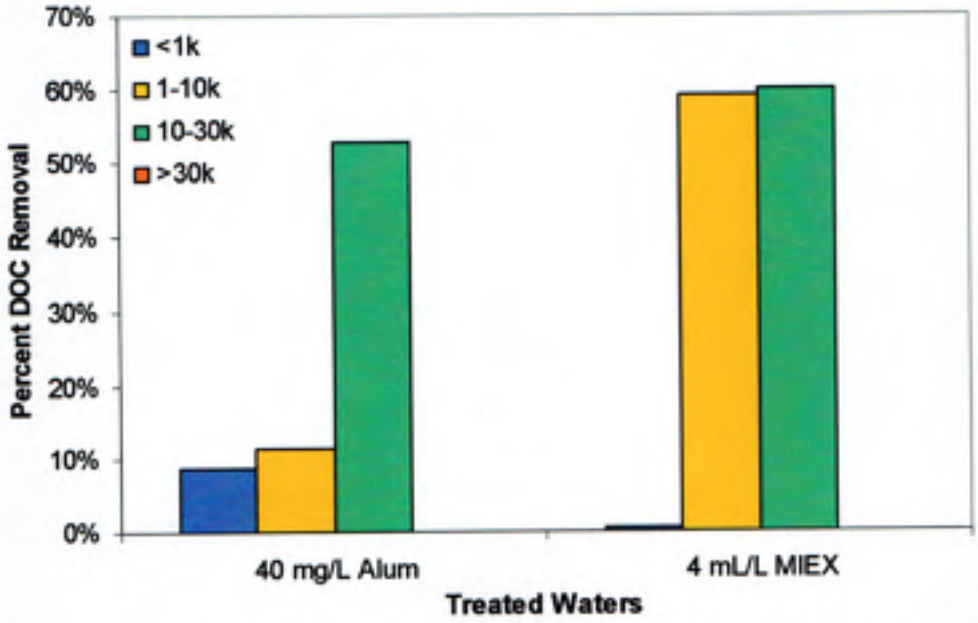

Figure 4.30 Impact of coagulation and treatment with MIEX on the removal of different molecular weight fractions for SL water

4.7 SUMMARY OF IMPACT OF COAGULATION AND TREATMENT WITH MIEX ON UV ABSORBANCE, DOC, THM4FP, HAA9FP

Figure 4.31 summarizes the impact of coagulation on the removal of UV absorbance, DOC, THM4FP, and HAA9FP for all four waters. Percent removal by coagulation tended to increase as the raw water SUVA increased, demonstrating that coagulation preferentially removes UV-absorbing, humic substances. Figure 4.32 summarizes the corresponding impact of treatment with MIEX on the removal of UV absorbance, DOC, THM4FP and HAA9FP. For all four waters, treatment with MIEX showed greater percent removals for all parameters compared to coagulation. Similar to coagulation, treatment with MIEX showed greater percent removals as the raw water SUVA increased. This trend is confounded, somewhat, by the fact that the raw waters with the lowest SUVA values (i.e. SL water and CL water) also had the highest concentration of anionic species, based on the bromide ion concentrations which are presumed to be an indicator of the total dissolved solids in the water. Therefore, it is not certain whether the performance of MIEX in these waters was reduced more by the high anionic composition of the waters or by the more hydrophilic nature of the DOC. The removal of THM4FP and HAA9FP is also confounded by the extent of bromine incorporation into the DBPs. For waters in which there were high bromide ion concentrations and little bromide removal, e.g. SL water and CL water, there was little change in the concentration of the bromine-containing DBP species. For some species, the concentrations actually increased as a result of alum and MIEX treatment. In general, percent removal by coagulation and treatment with MIEX displayed a removal pattern of: UV254 > HAA9FP > DOC ≈ THM4FP.

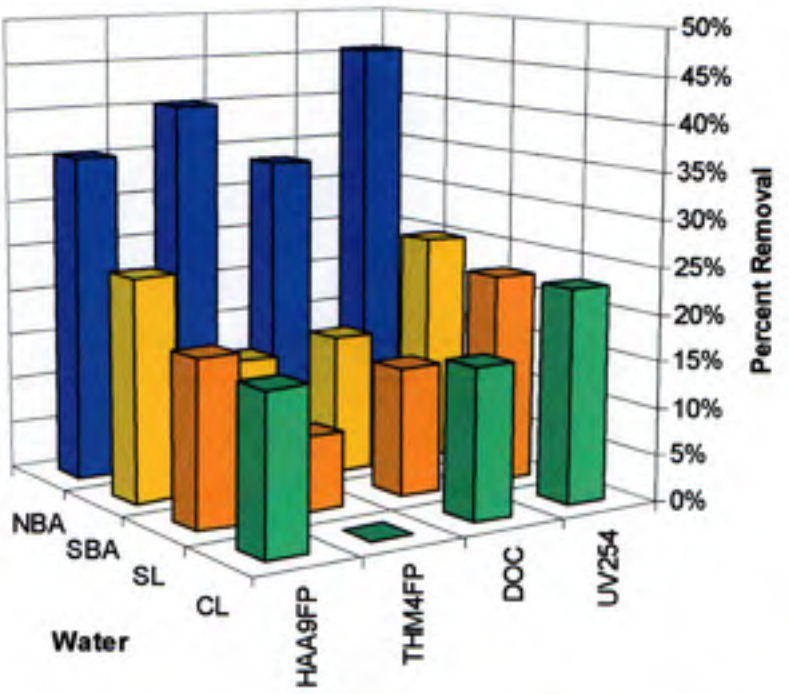

Figure 4.31 Impact of coagulation on removal of UV absorbance, DOC, THM4FP, and HAA9FP for all four waters

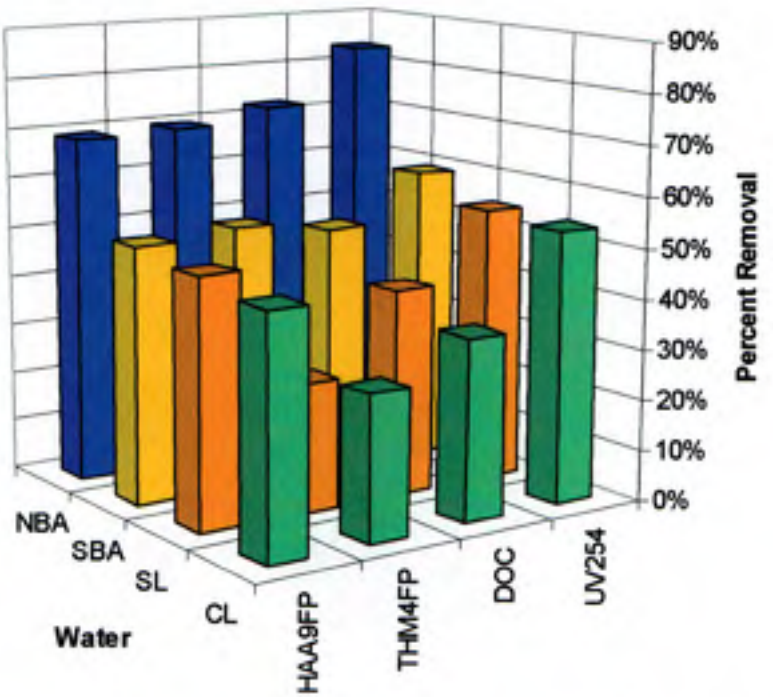

Figure 4.32 Impact of treatment with MIEX on removal of UV absorbance, DOC, THM4FP, and HAA9FP for all four waters

4.8 OTHER ION EXCHANGE RESINS: EQUILIBRIUM STUDIES

MIEX resin was compared with three traditional anion exchange resins (M-T, A641, and SIR) and two non-ionic resins (XAD761 and XAD7HP) for removal of NOM. Properties of these resins were shown in Table 3.2. Equilibrium (capacity) studies were conducted using NBA water and SL water because they both had appreciable concentrations of DOC. It was assumed that equilibrium was reached after seven days of continuous mixing. Both the removal of UV absorbance and the removal of DOC were used to evaluate the capacity of the resins for NOM. Neither XAD761 nor XAD7HP showed any removal of UV-absorbing materials or DOC. No additional pre-treatment beyond rinsing with DOFW was performed on any of the resins, and it may be that further pre-treatment was necessary for these non-ionic resins.

4.8.1 Impact on UV Absorbance

Figure 4.33 displays the impact of ion exchange treatment on UV absorbance capacity for NBA water. MIEX and M-T are polyacrylic-based resins whereas A641 and SIR are polystyrene-based resins. Figure 4.33 indicates that the polystyrene resins have a greater capacity for UV-absorbing substances than the polyacrylic resins. Researchers have observed that the ability of a resin to remove NOM increases as the percent water content of the resin increases, regardless of the resin structure (Fu and Symons 1990, Bolto et al. 2002a). If the percent water content of the resins (see Table 3.2) is compared to their capacity for UV-absorbing substances, a direct association between increasing water content and capacity for UV-absorbing materials is observed. The water content of MIEX was not available, but results from the capacity studies suggest that MIEX may have a lower water content than M-T.

Figure 4.34 displays the impact of ion exchange treatment on UV absorbance capacity for SL water. Again, the polystyrene resins have a greater capacity for UV-absorbing substances compared to the polyacrylic resins. The capacity of the ion exchange resins for UV-absorbing materials in SL water does not appear to be as strongly associated with the water content of the resin as was the case for NBA water. The results

shown in Figures 4.33 and 4.34 demonstrate that the capacity for UV-absorbing substances increases with increasing resin dose for all resins. For both NBA water and SL water, a substantial amount of UV-absorbing material was removed by the lowest resin dose. Both figures indicate that MIEX had the lowest capacity for UV-absorbing substances as compared to the other three resins evaluated.

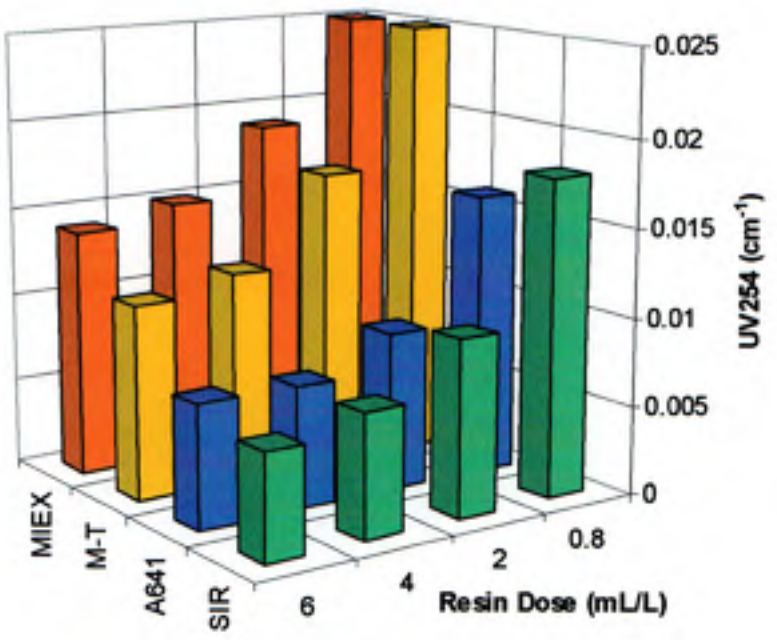

Figure 4.33 Impact of ion exchange treatment on UV absorbance capacity for NBA water (raw water UV254 = 0.193 cm^{-1})

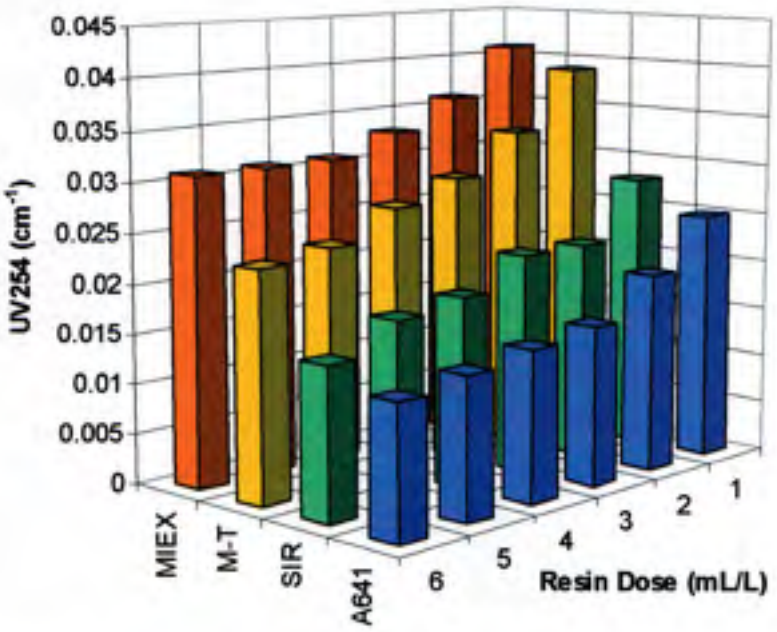

Figure 4.34 Impact of ion exchange treatment on UV absorbance capacity for SL water (raw water UV254 = 0.102 cm^{-1})

4.8.2 Impact on DOC

Figure 4.35 displays the impact of ion exchange treatment on DOC removal capacity for NBA raw water. For all resins, the DOC removal capacity increased with increasing resin dose, with a substantial amount of DOC removal at the lowest resin dose. Figure 4.35 indicates that the polystyrene resins have a greater DOC removal capacity than the polyacrylic resins. For the polystyrene resins, SIR has a higher water content than A641 and has the highest capacity for DOC.

Figure 4.36 shows the impact of ion exchange treatment on DOC removal capacity for SL raw water. Similar trends can be noted between Figures 4.35 and 4.36. For both NBA water and SL water, SIR has the highest capacity for DOC while MIEX has the lowest capacity. The unusually high value of the DOC concentration for the 1 mL/L M-T resin dose is likely due to analytical error.

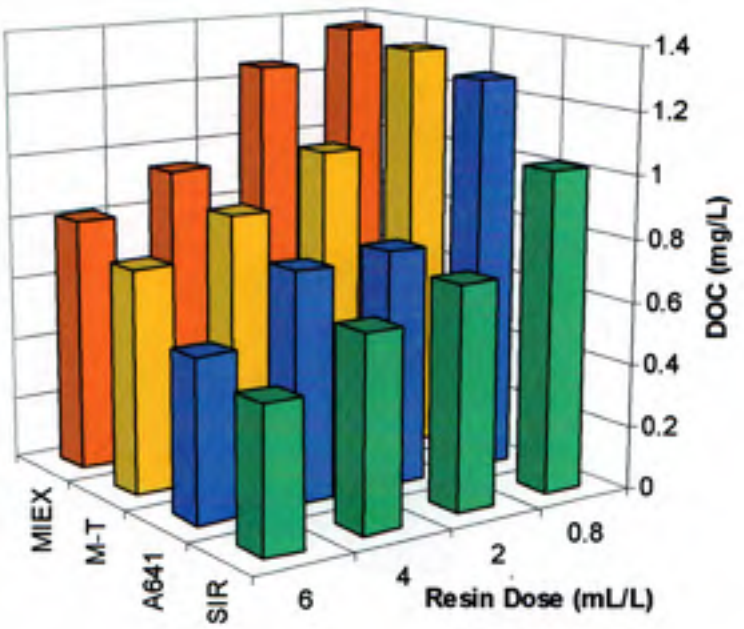

Figure 4.35 Impact of ion exchange treatment on DOC removal capacity for NBA water (raw water DOC 5.1 mg/L)

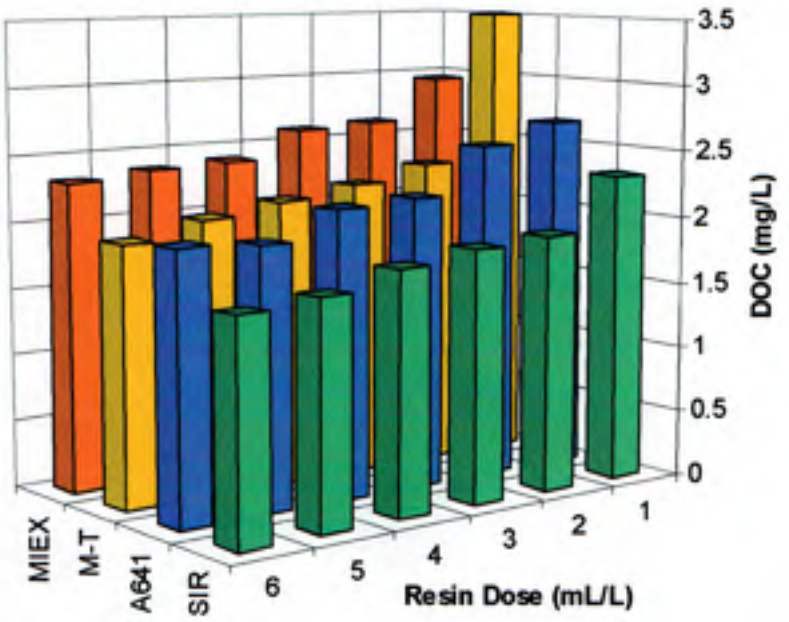

Figure 4.36 Impact of ion exchange treatment on DOC removal capacity for SL water (raw water DOC 5.1 mg/L)

4.8.3 Linearized Freundlich Isotherms

Figure 4.37 shows linearized Freundlich isotherms based on the DOC removal results for NBA water. A similar figure for SL water is contained in Appendix G. The equation for the Freundlich isotherm is

$$q_e = k \cdot C_e^n \tag{4-1}$$

where q_e is the mass of DOC adsorbed per mass of resin (e.g. mg-C/g-resin) and C_e is the equilibrium concentration of DOC remaining in solution (e.g. mg-C/L). The data conform reasonably well to the Freundlich model. Since the isotherm for the SIR resin is above the other isotherms, the capacity of the SIR resin for DOC is greater than the other resins. Since the isotherm for the MIEX resin is below the other isotherms, it has the lowest capacity for DOC compared to the other three resins. This is consistent with the trend illustrated in Figure 4.36. The linearized Freundlich isotherm for SL water (see Appendix G) gives similar results.

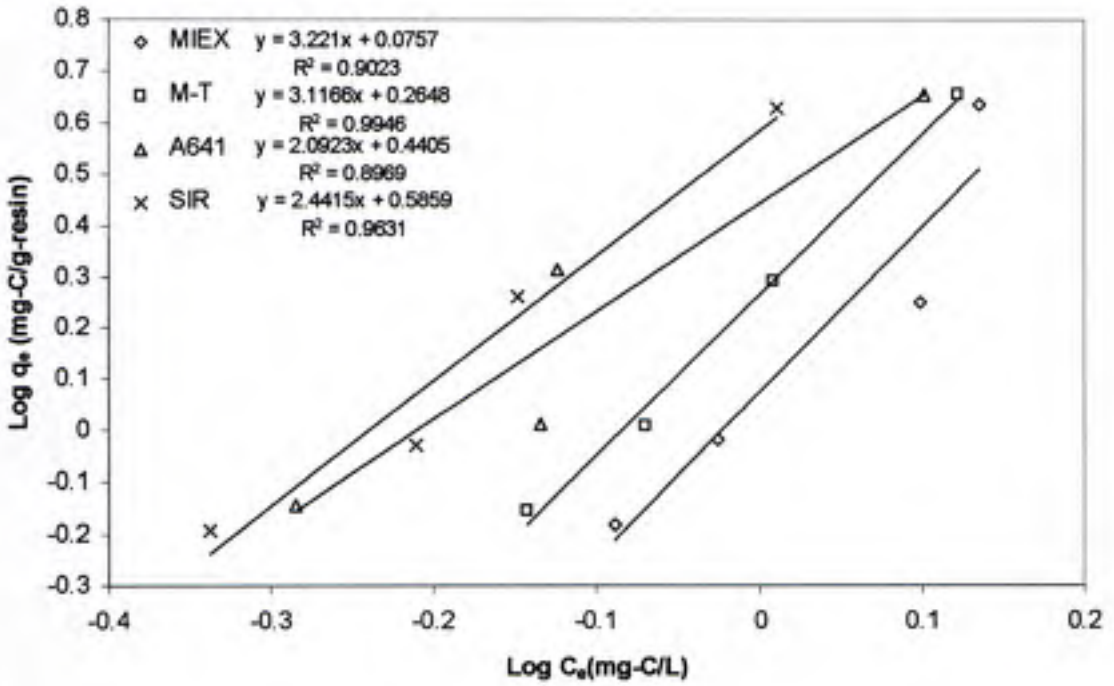

Figure 4.37 Linearized Freundlich isotherms based on DOC removal for NBA water

4.9 OTHER ION EXCHANGE RESINS: KINETIC STUDIES

Due to the smaller size of the MIEX resin, it was expected that the MIEX resin would remove NOM at a faster rate than the other ion exchange resins.

4.9.1 Impact on UV Absorbance

Figure 4.38 shows the rate of removal of UV-absorbing substances by ion exchange treatment for NBA water. During the first 20 minutes of mixing, the MIEX resin displayed rapid removal of UV absorbance compared to the other three resins. As time increased, the difference in the rate of removal of UV absorbance between MIEX and the other resins became less pronounced. Based on the results of the kinetic study for NBA water, it was decided that more samples needed to be taken during the first 20 minutes of mixing. Figure 4.39 shows the rate of removal of UV-absorbing substances by ion exchange treatment for SL water. Figure 4.39 verifies that MIEX removes UV-absorbing substances at a much quicker rate than the other resins. Appendix H contains additional kinetic results for SL water.

Figure 4.40 further illustrates the impact of ion exchange treatment on the rate of UV absorbance removal for SL water. The kinetic study was conducted with two resin doses to see if resin dose has any affect on the rate of UV absorbance removal. Figure 4.40 shows that MIEX has a greater rate of UV absorbance removal between zero and 60 minutes for both doses. The rates of UV absorbance removal become comparable for all four resins after 60 minutes.

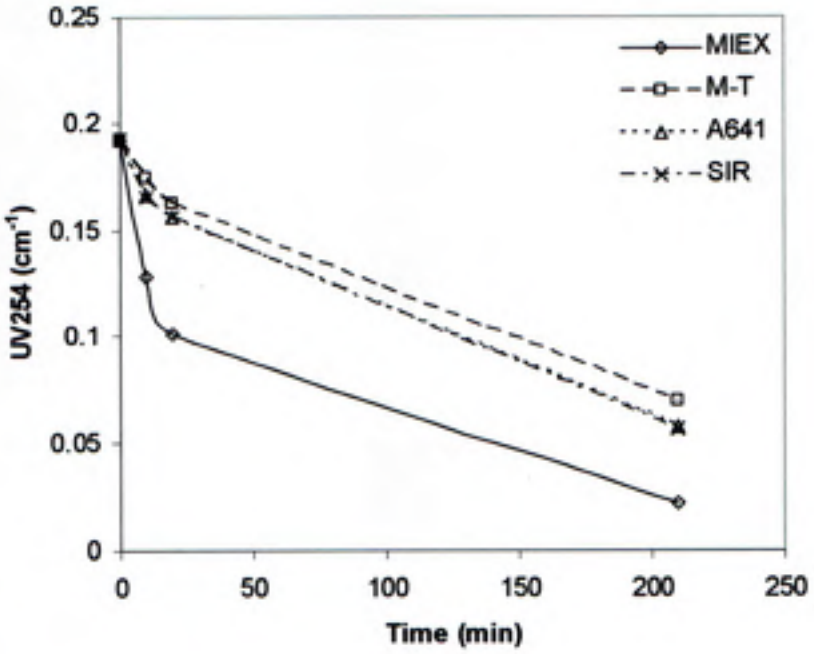

Figure 4.38 Rate of removal of UV-absorbing substances by ion exchange treatment for NBA water (2 mL/L resin)

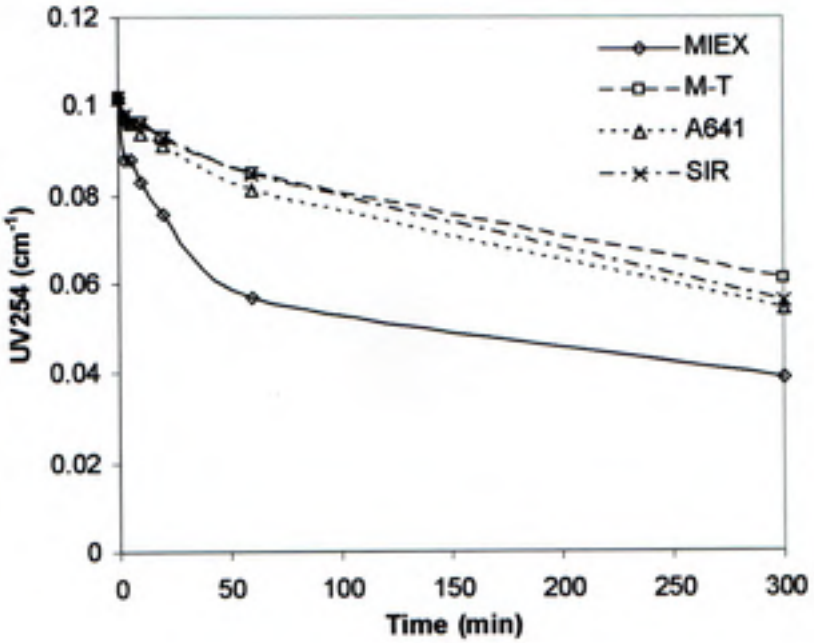

Figure 4.39 Rate of removal of UV-absorbing substances by ion exchange treatment for SL water (1 mL/L resin)

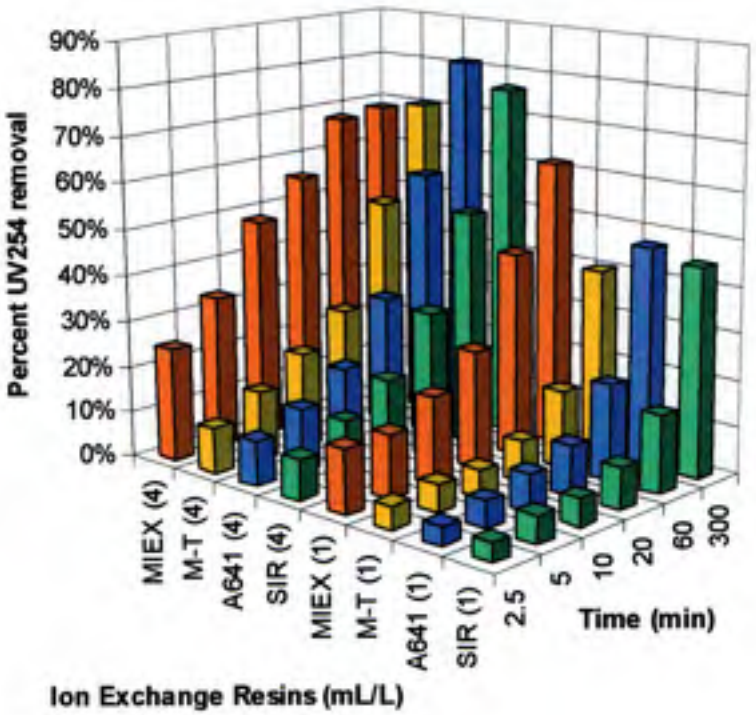

Figure 4.40 Impact of ion exchange treatment on the rate of UV absorbance removal for SL water (raw water UV254 = 0.102 cm^{-1})

4.9.2 Impact on DOC

Figures 4.41 and 4.42 display the rate of DOC removal by ion exchange treatment for NBA water and SL water, respectively. Similar to the UV results, these figures show that the rate of DOC removal by MIEX is greater than for the other resins in the 20 to 60 minute range. The apparent increase in DOC concentration shown in Figure 4.42 at the low contact times for some of the resins is probably due to analytical error or poor solid-liquid separation.

Figure 4.43 illustrates the impact of ion exchange treatment on the rate of DOC removal for SL water for two different resin doses. For the low resin dose of 1 mL/L, MIEX is the only resin that shows any substantial DOC removal between zero and 60

minutes. For the 4 mL/L resin dose, MIEX has a faster rate of DOC removal during the first 20 to 60 minutes of mixing than the other ion exchange resins.

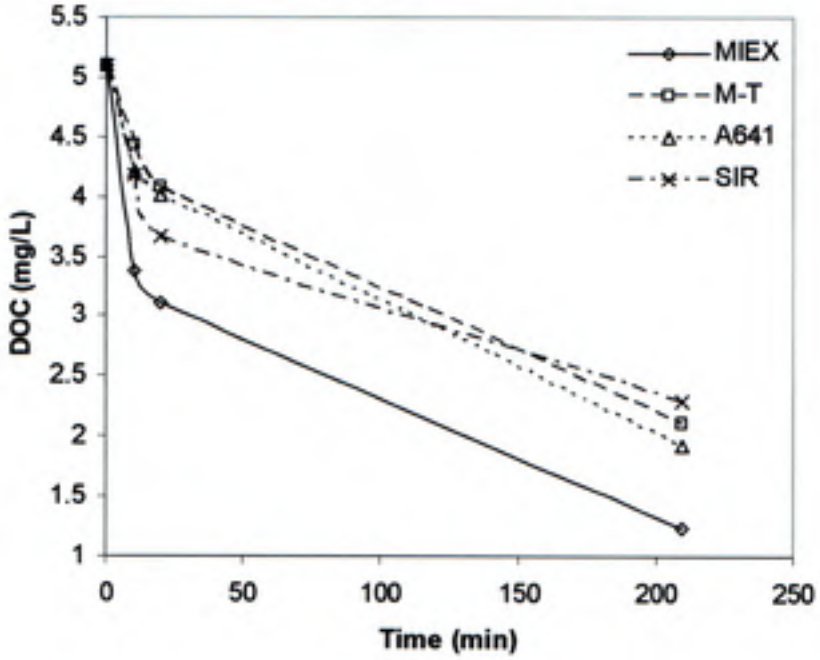

Figure 4.41 Rate of DOC removal by ion exchange treatment for NBA water (2 mL/L resin)

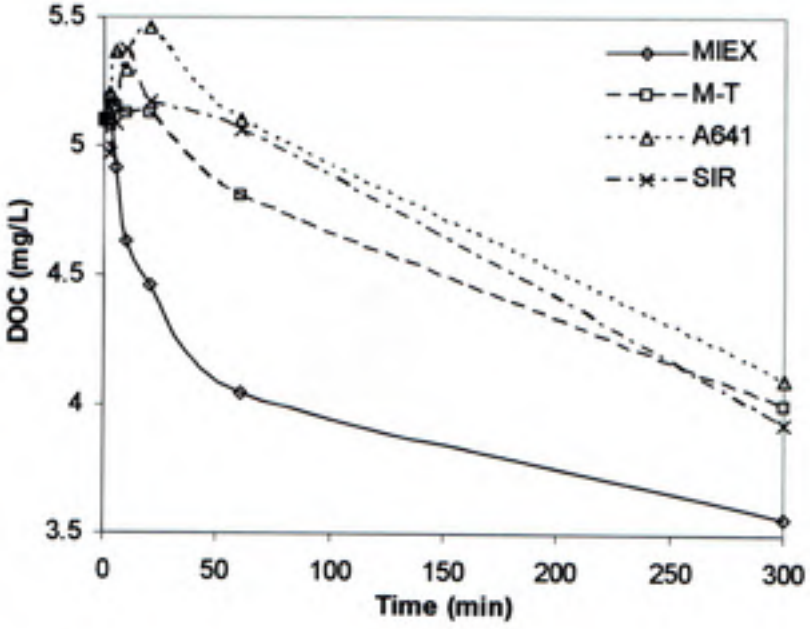

Figure 4.42 Rate of DOC removal by ion exchange treatment for SL water (1 mL/L resin)

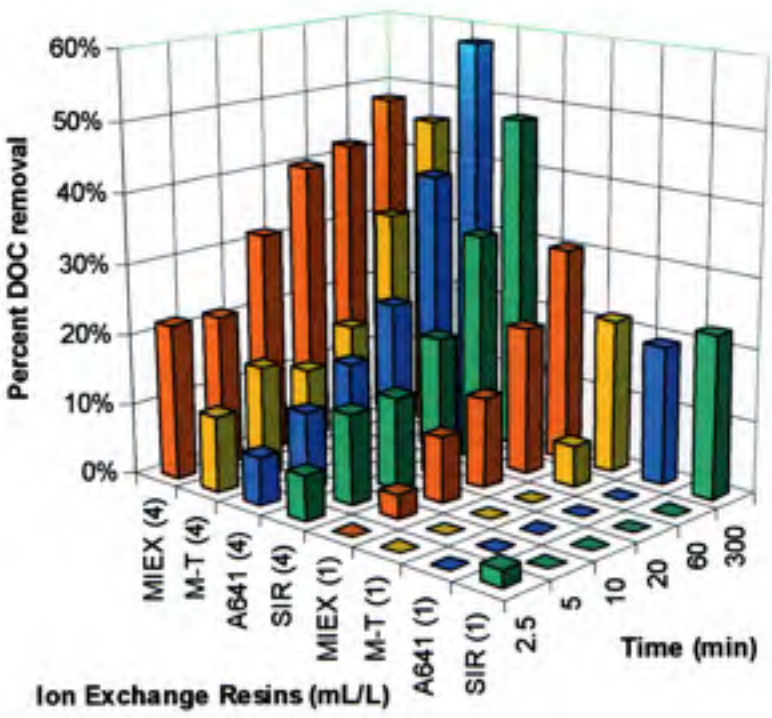

Figure 4.43 Impact of ion exchange treatment on the rate of DOC removal for SL water (raw water DOC 5.1 mg/L)

4.9.3 Impact on Bromide

During the kinetic studies, samples were taken at various times for bromide analysis. Table 4.4 shows the impact of ion exchange treatment on bromide removal for all of the kinetic studies conducted. For all resins, the percent removal of bromide was greater in NBA water than in SL water. This was expected because NBA water had a lower alkalinity and a lower concentration of bromide (and an assumed lower TDS concentration) than SL water. Johnson and Singer (2003) have shown these conditions to be conducive to bromide removal by treatment with MIEX. Mixing time did not seem to have an impact on bromide removal. This suggests that the ion exchange mechanism for bromide exchange happens on short time scales (i.e. on the order of minutes). The A641

resin has the greatest affinity for bromide, as illustrated by greater than 50% removal of bromide for both waters. The M-T and SIR resins removed bromide to similar extents, approximately 15-30%. MIEX showed the least preference for bromide based on these studies.

Table 4.4 Impact of ion exchange treatment on bromide removal

Resin	Water	Bromide (µg/L)	Resin Dose (mL/L)	Time (min)	Percent Bromide Removal
MIEX	NBA	76	2	20	13
MIEX	NBA	76	2	210	14
MIEX	SL	540	4	20	11
MIEX	SL	540	4	60	11
M-T	NBA	76	2	20	28
M-T	NBA	76	2	210	16
M-T	SL	540	4	20	20
M-T	SL	540	4	60	15
A641	NBA	76	2	20	50
A641	NBA	76	2	210	59
A641	SL	540	4	20	52
A641	SL	540	4	60	52
SIR	NBA	76	2	20	30
SIR	NBA	76	2	210	16
SIR	SL	540	4	20	20
SIR	SL	540	4	60	13

4.10 SUMMARY OF ION EXCHANGE STUDIES

Based on the results of Section 4.8, the SIR resin appears to have the greatest capacity for UV-absorbing substances and DOC among the four resins studied. The MIEX resin had the lowest capacity. In general, the two polystyrene resins had a greater capacity for UV-absorbing substances and DOC compared to the polyacrylic resins. The capacities were directly related to the water content of the resins. In waters with a high SUVA, all of the ion exchange resins had a similar capacity for UV-absorbing substances and overall DOC, but as the SUVA of the water decreased, the capacity of the resins for

overall DOC decreased to a greater degree than their capacity for UV-absorbing materials.

Kinetic studies verified that MIEX had a higher rate of removal of UV-absorbing materials and DOC compared to the other resins, presumably because of its smaller size. The other three resins all exhibited similar kinetics. Results from the kinetic studies also indicate that A641 had the greatest selectivity for bromide.

CHAPTER 5

CONCLUSIONS

5.1 CONCLUSIONS

The primary objective of this research was to compare alum coagulation with anion exchange for removal of DBP precursors. Several anion exchange resins were evaluated for their capacity to remove NOM and bromide and for the rate at which they removed these DBP precursors. Treatment with MIEX was the primary focus of this study. The conclusions of this research are as follows:

- Treatment with MIEX removes UV-absorbing substances and DOC to a greater extent than coagulation with alum. Treatment with MIEX and treatment with MIEX followed by coagulation removes UV-absorbing material and DOC to a similar degree. This suggests that treatment with MIEX removes a wide range of DOC, including the fraction of DOC preferentially removed by coagulation.
- Treatment with MIEX was most effective at removing UV-absorbing substances and DOC in raw waters with a high SUVA and a low anionic composition. It is unclear whether the presence of hydrophilic NOM or high anionic composition had a greater impact on reducing the effectiveness of treatment with MIEX in raw waters with low SUVA values. Coagulation was most effective in raw waters with a high SUVA, low alkalinity, and high initial DOC concentration.
- Treatment with MIEX removed the HPOA, TPHA, and HPIA fractions of DOC to a greater extent than coagulation. In waters with a high SUVA, treatment with MIEX removed all organic acid fractions to a similar degree. As the dose of the MIEX resin increased, treatment with MIEX removed more of each of the organic acid fractions. Treatment with MIEX removed the <1k, 1-10k, and 10-30k fractions of DOC to a greater extent than coagulation.
- Treatment with MIEX reduced THM4FP and HAA9FP in all waters. Treatment with MIEX and treatment with MIEX followed by coagulation removed THM4FP and HAA9FP to a similar extent. Coagulation was only effective at reducing THM4FP and HAA9FP in waters with a high SUVA, and was not as effective as treatment with

MIEX. For both treatment with MIEX and coagulation, the general trend of removal was as follows: UV254 > HAA9FP > DOC ≈ THM4FP

- Treatment with MIEX removed bromide from all four raw waters investigated. The percent removal of bromide increased as the raw water alkalinity decreased and the bromide ion concentration decreased. Coagulation did not remove bromide.
- As the Br/TOC ratio of the raw water increased, there was a pronounced shift toward formation of the more brominated THM and HAA species following chlorination. After treatment with MIEX, and to a lesser extent after coagulation, there was also a shift to the more brominated THM and HAA species following chlorination. This is attributed to an increase in the Br/TOC ratio following treatment (i.e. TOC was removed to a much greater degree than bromide). In some cases, the concentration of brominated DBP species was greater after treatment with MIEX than in the raw water.
- Bromine incorporation into trihalomethanes, trihaloacetic acids, and dihaloacetic acids was approximately equal.
- Polystyrene-based anion exchange resins removed UV-absorbing materials and DOC to a greater extent than polyacrylic-based anion exchange resins. This is assumed to be a result of the higher water content of the former.
- MIEX removed UV-absorbing substances and DOC faster than the other anion exchange resins examined.

5.2 RECOMMENDATIONS FOR FURTHER RESEARCH

Further research relating to anion exchange can be divided into additional bench-scale experiments, pilot-scale testing, and mathematical modeling of NOM removal by ion exchange.

The primary objectives of the bench-scale experiments would be to quantify the selectivity of MIEX and other anion exchange resins for different fractions of NOM and various anions of interest in natural waters. Treatment with MIEX was least effective at removing DBP precursors in SL water and CL water which had low SUVA values, high alkalinities, and high bromide ion concentrations. Therefore, it would be useful to

determine whether the presence of hydrophilic NOM or competition by other anions with NOM or both resulted in the decrease in treatment performance with MIEX. This can be explored in well-defined model solutions in which each of the effects is isolated. It would also be useful to determine the quantitative selectivity of MIEX resin for a host of anions present in natural water including carbonate, bicarbonate, chloride, bromide, sulfate, and nitrate. Employing other techniques for characterization of NOM, such as size exclusion chromatography, could provide more insight into the properties of NOM that influence MIEX treatability and the nature of the resultant DOC (i.e. the organic acids and molecular weight fractions remaining after MIEX treatment). Using equilibrium (capacity) and kinetic studies, it would be interesting to further investigate other ion exchange resins for removal of NOM.

The purpose of pilot-plant testing would be to validate bench-scale results and optimize the process. Important parameters to investigate related to pilot-scale treatment with MIEX include resin dose, contact time, recycle ratio, regeneration effectiveness, and brine re-use (i.e. for regeneration). A comprehensive investigation of resin dose, contact time, and recycle ratio would provide insight to optimizing the process for removal of DBP precursors. A long-term pilot-study would also allow for an analysis of the effectiveness of resin regeneration. Understanding brine re-use is important because the less brine that requires treatment or disposal lessens the impact of anion exchange technology on the environment and reduces the overall cost of ion exchange treatment.

The ultimate goal of the bench-scale experiments and pilot-scale testing would be to develop a mathematical model for NOM removal by ion exchange. Important inputs to the model would include the concentration and characteristics of the NOM, the anionic composition of the water, and general water quality parameters, such as pH and turbidity. The model could then be used to predict the removal of NOM by ion exchange in other waters with different water qualities and different operating conditions.

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Appendix A
Reproducibility of MIEX Experiments

This appendix contains the results of a MIEX reproducibility study that was conducted with NBA water in order to verify the precision of experiments with MIEX. Details of the experimental procedure are given in § 3.3.2. The results of this study are shown in Table A.1.

Table A.1 Results of MIEX reproducibility study

MIEX dose	TOC	DOC	UV254
mL/L	mg/L	mg/L	cm^{-1}
4	1.5	1.6	0.043
4	1.8	1.5	0.040
4	1.6	1.5	0.042
4	1.7	1.5	0.042
4	1.9	1.4	0.042
4	1.6	1.5	0.041
Mean	1.7	1.5	0.042
Variance	0.014	0.004	0.000
Standard Deviation	0.12	0.06	0.001
Coefficient of Variation	7%	4%	2%

Appendix B
Preliminary Jar-Tests Experiments

Preliminary jar-test experiments were conducted for each raw water to determine appropriate doses of coagulant and MIEX. Details of the experimental procedures and the criteria for choosing the appropriate coagulant or MIEX dose can be found in § 3.3. Tables B.1.1-B.1.4 show the results of preliminary coagulation experiments for the four waters tested. Tables B.2.1-B.2.4 show the results of preliminary experiments with MIEX on these same four waters. Tables B.3.1-B.3.4 show the results of preliminary coagulation experiments using MIEX-treated water.

B.1 Coagulation with Alum

Table B.1.1 Summary of preliminary coagulation experiments for NBA water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
raw	7.54	9.5	0.183	5.3	5.1	3.6
30	7.49	9.7	0.133	4.9	3.7	3.6
40	7.40	2.1	0.111	4.0	3.3	3.3
50	7.37	1.8	0.100	3.8	3.2	3.1
60	7.36	1.4	0.088	3.2	3.0	2.9

Table B.1.2 Summary of preliminary coagulation experiments for CL water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
raw	8.63	7.0	0.074	2.3	2.2	3.4
10	7.61	5.6	0.065	2.2	2.1	3.2
15	7.72	3.1	0.061	2.2	2.0	3.1
20	7.53	1.2	0.054	1.9	2.0	2.8
25	7.45	0.8	0.049	1.8	1.8	2.7
30	7.35	0.8	0.043	1.7	1.7	2.6
35	7.30	0.5	0.040	1.7	1.6	2.5

Table B.1.3 Summary of preliminary coagulation experiments for SBA water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
raw	7.77	6.0	0.064	1.9	1.9	3.4
5	7.57	1.9	0.054	1.4	1.4	4.0
10	7.46	1.7	0.045	1.5	1.3	3.5
15	7.36	1.1	0.039	1.3	1.2	3.3
20	7.25	0.8	0.032	1.1	1.0	3.1
25	7.12	0.7	0.029	1.0	1.0	3.0
30	7.07	1.0	0.025	1.0	0.9	2.8

Table B.1.4 Summary of preliminary coagulation experiments for SL water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
raw	8.10	5.5	0.102	5.2	5.1	2.0
10	7.70	1.9	0.094	5.1	4.8	1.9
20	7.70	0.8	0.087	5.0	4.7	1.8
30	7.57	0.7	0.083	4.8	4.2	2.0
35	7.50	0.7	0.080	4.7	4.4	1.8
40	7.47	0.7	0.078	4.4	4.0	1.9

B.2 Treatment with MIEX

Table B.2.1 Summary of preliminary experiments with MIEX for NBA water

MIEX dose	UV254 5 min	UV254 10 min	UV254 20 min	UV254 30 min	TOC	DOC	SUVA‡	pH	Turbidity	Bromide
mL/L	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$		NTU	µg/L
raw	-	-	-	0.193	5.5	4.9	4.0	7.09	20.0	76
2	0.091	0.08	0.065	0.070	2.5	2.2	3.2	7.20	17.5	62
4	0.043	0.054	0.037	0.033	1.6	1.4	2.3	7.29	16.0	51
6	0.048	0.035	0.018	0.020	1.2	1.2	1.7	7.34	14.5	45

‡Based on 30 minute UV254 value

Table B.2.2 Summary of preliminary experiments with MIEX for CL water

MIEX dose	UV254 5 min	UV254 10 min	UV254 20 min	UV254 30 min	TOC	DOC	SUVA‡	pH	Turbidity	Bromide
mL/L	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$		NTU	µg/L
raw	0.074	0.074	0.074	0.074	2.3	2.2	3.4	8.63	7.0	240
0.5	0.055	0.058	0.052	0.054	1.6	1.7	3.2	8.49	4.8	220
1	0.054	0.048	0.04	0.038	1.4	1.5	2.6	8.49	3.5	220
2	0.041	0.036	0.027	0.026	1.1	1.2	2.2	8.44	3.3	200
3	0.034	0.026	0.016	0.015	0.9	0.9	1.6	8.30	2.8	170

‡Based on 30 minute UV254 value

Table B.2.3 Summary of preliminary experiments with MIEX for SBA water

MIEX dose	UV254 5 min	UV254 10 min	UV254 20 min	UV254 30 min	TOC	DOC	SUVA‡	pH	Turbidity	Bromide
mL/L	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$		NTU	µg/L
raw	0.064	0.064	0.064	0.064	1.9	1.9	3.4	7.77	6.0	83
0.5	0.056	0.053	0.047	0.049	1.3	1.2	4.0	7.84	4.7	67
1	0.052	0.044	0.039	0.04	1.0	1.0	4.1	7.78	3.0	61
2	0.044	0.037	0.03	0.027	0.7	0.6	4.2	7.64	3.2	42
3	0.037	0.028	0.019	0.017	0.5	0.4	4.0	7.53	2.9	34

‡Based on 30 minute UV254 value

Table B.2.4 Summary of preliminary experiments with MIEX for SL water

MIEX dose	UV254 5 min	UV254 10 min	UV254 20 min	UV254 30 min	TOC	DOC	SUVA‡	pH	Turbidity	Bromide
mL/L	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$		NTU	µg/L
raw	0.102	0.102	0.102	0.102	5.2	5.1	2.0	8.10	5.5	540
2	0.057	0.049	0.044	0.048	3.4	3.3	1.5	8.14	1.4	520
4	0.044	0.037	0.034	0.036	2.8	2.8	1.3	8.09	1.2	480
6	0.041	0.034	0.031	0.032	2.6	2.7	1.2	8.10	1.2	440

‡Based on 30 minute UV254 value

B.3 Treatment with MIEX followed by Coagulation with Alum

Table B.3.1 Preliminary coagulation experiments for MIEX-treated NBA water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
5 mL/L MIEX	6.88	10.4	0.032	1.5	1.4	2.3
6	6.83	10.1	0.026	1.9	1.4	1.9
8	6.82	9.9	0.025	1.5	1.3	1.9
10	6.78	7.1	0.023	1.3	1.3	1.8
12	6.79	5.0	0.021	1.5	1.3	1.6
16	6.88	1.8	0.019	1.4	1.3	1.5
20	6.95	1.7	0.015	1.3	1.2	1.3

Table B.3.2 Preliminary coagulation experiments for MIEX-treated CL water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
2 mL/L MIEX	8.32	2.1	0.034	1.5	1.6	2.2
4	7.89	1.9	0.031	1.3	1.6	1.9
6	7.82	1.8	0.030	1.5	1.5	2.0
8	7.75	1.8	0.028	1.5	1.5	1.9

Table B.3.3 Preliminary coagulation experiments for MIEX-treated SBA water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
2 mL/L MIEX	7.69	1.8	0.026	1.0	0.9	2.8
1	7.66	1.7	0.026	1.0	1.1	2.4
3	7.61	1.8	0.023	1.0	0.9	2.5
5	7.53	1.8	0.019	1.1	0.9	2.1

Table B.3.4 Preliminary coagulation experiments for MIEX-treated SL water

Alum dose	pH	Turbidity	UV254	TOC	DOC	SUVA
mg/L		NTU	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$
4 mL/L MIEX	8.16	1.7	0.046	3.2	3.0	1.5
5	7.95	1.7	0.045	3.5	3.0	1.5
10	7.85	1.8	0.042	3.4	3.1	1.3
15	7.74	1.7	0.043	3.4	3.2	1.4
20	7.69	1.1	0.041	3.4	3.0	1.3

Appendix C
Summary of Raw and Treated Water Results

This appendix contains water quality data for all raw waters and treated waters. Tables C.1.1-C.1.4 contain general water quality data, Tables C.2.1-C.2.4 display the concentration of individual THM species, and Tables C.3.1-C.3.4 show the concentration of individual HAA species for all raw waters and all treated waters.

C.1 General Water Quality

Table C.1.1 Summary for water quality data for NBA water

Waters	UV254	TOC	DOC	SUVA	Br^-	THM4FP	HAA9FP	Cl_2**
	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$	µg/L	µg/L	µg/L	mg/L
Raw (149 mg/L as $CaCO_3$)	0.193	5.5	5.1	3.8	76	294	224	7.2
60 mg/L Alum	0.105	3.5	3.4	3.1	73	176	145	4.2
5 mL/LMIEX	0.032	1.5	1.4	2.3	55	90.1	69.5	1.9
5 mL/L MIEX + 16 mg/L Alum	0.029	1.4	1.2	2.4	56	72.7	62.3	1.7

**Cl_2 consumed

Table C.1.2 Summary for water quality data for CL water

Waters	UV254	TOC	DOC	SUVA	Br^-	THM4FP	HAA9FP	Cl_2**
	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$	µg/L	µg/L	µg/L	mg/L
Raw (92 mg/L as $CaCO_3$)	0.074	2.3	2.5	3.0	240	150	65.3	3.4
20 mg/L Alum	0.057	2.1	2.1	2.7	240	150	54.4	3.1
2 mL/LMIEX	0.034	1.5	1.6	2.1	200	107	34.7	3.3
2 mL/L MIEX + 4 mg/L Alum	0.032	1.7	1.7	1.8	190	102	32.6	2.1

**Cl_2 consumed

Table C.1.3 Summary for water quality data for SBA water

Waters	UV254	TOC	DOC	SUVA	Br^-	THM4FP	HAA9FP	Cl_2**
	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$	µg/L	µg/L	µg/L	mg/L
Raw (57 mg/L as $CaCO_3$)	0.064	1.9	1.9	3.4	83	111	90.5	2.2
10 mg/L Alum	0.048	2.0	1.6	3.0	85	95.3	68.8	2.3
2 mL/LMIEX	0.026	1.0	0.9	2.8	46	52.7	44.3	1.6
2 mL/L MIEX + 5 mg/L Alum	0.020	1.0	0.8	2.6	43	39.5	41.3	1.6

**Cl_2 consumed

Table C.1.4 Summary for water quality data for SL water

Waters	UV254	TOC	DOC	SUVA	Br^-	THM4FP	HAA9FP	Cl_2**
	cm^{-1}	mg/L	mg/L	$Lmg^{-1}m^{-1}$	µg/L	µg/L	µg/L	mg/L
Raw (188 mg/L as $CaCO_3$)	0.102	5.2	5.1	2.0	540	283	127	4.1
40 mg/L Alum	0.079	4.4	4.4	1.8	530	261	105	3.9
4 mL/LMIEX	0.046	3.2	3.0	1.5	460	210	64.7	2.9
4 mL/L MIEX + 20 mg/L Alum	0.043	3.0	3.0	1.4	470	204	62.0	2.9

**Cl_2 consumed

C.2 THM Concentrations

Table C.2.1 Summary of individual THM species concentrations for NBA water

Waters	Cl_3CH	$BrCl_2CH$	Br_2ClCH	Br_3CH	THM4
	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	262	25.4	4.9	2	294
60 mg/L Alum	141	25.8	7.6	2	176
5 mL/LMIEX	56.1	25.8	7.7	<1	90.1
5 mL/L MIEX + 16 mg/L Alum	42.1	22.0	8.1	<1	72.7

Table C.2.2 Summary of individual THM species concentrations for CL water

Waters	Cl_3CH	$BrCl_2CH$	Br_2ClCH	Br_3CH	THM4
	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	36.6	43.8	59.9	9.3	150
20 mg/L Alum	31.1	42.8	63.5	12.7	150
2 mL/LMIEX	17.7	29.2	46.6	13.2	107
2 mL/L MIEX + 4 mg/L Alum	15.7	27.4	45.4	13.7	102

Table C.2.3 Summary of individual THM species concentrations for SBA water

Waters	Cl_3CH	$BrCl_2CH$	Br_2ClCH	Br_3CH	THM4
	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	62.3	30.4	16.1	1.7	111
10 mg/L Alum	46.4	28.9	19.5	<1	95
2 mL/LMIEX	25.1	15.3	11.0	1.4	53
2 mL/L MIEX + 5 mg/L Alum	17.1	11.8	10.1	<1	40

Table C.2.4 Summary of individual THM species concentrations for SL water

Waters	Cl_3CH	$BrCl_2CH$	Br_2ClCH	Br_3CH	THM4
	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	38.0	70.9	128	46.2	283
40 mg/L Alum	26.2	60.1	121	53.4	261
4 mL/LMIEX	10.8	37.9	99.2	62.6	210
4 mL/L MIEX + 20 mg/L Alum	10.5	36.8	96.4	60.2	204

C.3 HAA Concentrations

Table C.3.1 Summary of individual HAA species concentrations for NBA water

Waters	ClAA	BrAA	Cl_2AA	BrClAA	Br_2AA	Cl_3AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	4	4	79.4	9.9	4	87.2	15.4	8.8	10.9	224
60 mg/L Alum	9.6	3.1	49.5	13.5	4.4	41.6	12.4	5.5	5.1	145
5 mL/LMIEX	5.1	2.8	18.5	8.6	4.6	12.2	7.1	5.4	5.2	69.5
5 mL/L MIEX + 16 mg/L Alum	5.5	2.8	14.7	7.8	4.8	9.3	6.7	5.5	5.2	62.3

Table C.3.2 Summary of individual HAA species concentrations for CL water

Waters	ClAA	BrAA	Cl_2AA	BrClAA	Br_2AA	Cl_3AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	<2	<2	12.0	14.5	10.5	9.1	8.1	6.1	3.1	65.3
20 mg/L Alum	<2	<2	8.5	11.9	10.5	6.6	5.9	5.6	3.3	54.4
2 mL/LMIEX	<2	<2	4.6	7.1	7.1	4.4	3.5	3.2	2.7	34.7
2 mL/L MIEX + 4 mg/L Alum	<2	<2	4.1	6.6	7.0	3.8	3.1	3.1	2.8	32.6

Table C.3.3 Summary of individual HAA species concentrations for SBA water

Waters	ClAA	BrAA	Cl_2AA	BrClAA	Br_2AA	Cl_3AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	2.6	<2	22.3	9.2	2.5	22.2	16.5	9.1	5.1	90.5
10 mg/L Alum	<2	<2	14.9	8.0	2.9	13.3	13.6	9.3	4.8	68.8
2 mL/LMIEX	<2	<2	8.5	3.9	<2	6.4	9.2	8.1	5.2	44.3
2 mL/L MIEX + 5 mg/L Alum	2.1	<2	6.7	3.6	<2	5.0	8.9	8.3	4.7	41.3

Table C.3.4 Summary of individual HAA species concentrations for SL water

Waters	ClAA	BrAA	Cl_2AA	BrClAA	Br_2AA	Cl_3AA	$BrCl_2AA$	Br_2ClAA	Br_3AA	HAA9
	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Raw	<2	3.2	11.4	20.7	26.9	4.7	16.1	23.1	20.1	127
40 mg/L Alum	<2	3.1	7.9	16.9	26.2	2.5	11.1	18.7	17.3	105
4 mL/LMIEX	<2	2.4	2.4	9.3	19.4	<2	5.8	10.8	12.6	64.7
4 mL/L MIEX + 20 mg/L Alum	<2	2.2	2.3	8.6	18.2	<2	5.6	10.4	12.7	62.0

Appendix D
THM and HAA Speciation of Chlorinated CL and SBA Waters

This appendix illustrates the impact of precursor removal on the speciation of THMs and HAAs in CL water and SBA water after chlorination. Figure D.1 and Figure D.2 show the impact of coagulation and treatment with MIEX on the speciation of THMs for SBA water and CL water, respectively. Figure D.3 and Figure D.4 show the impact of coagulation and treatment with MIEX on the speciation of HAAs for SBA water and CL water, respectively.

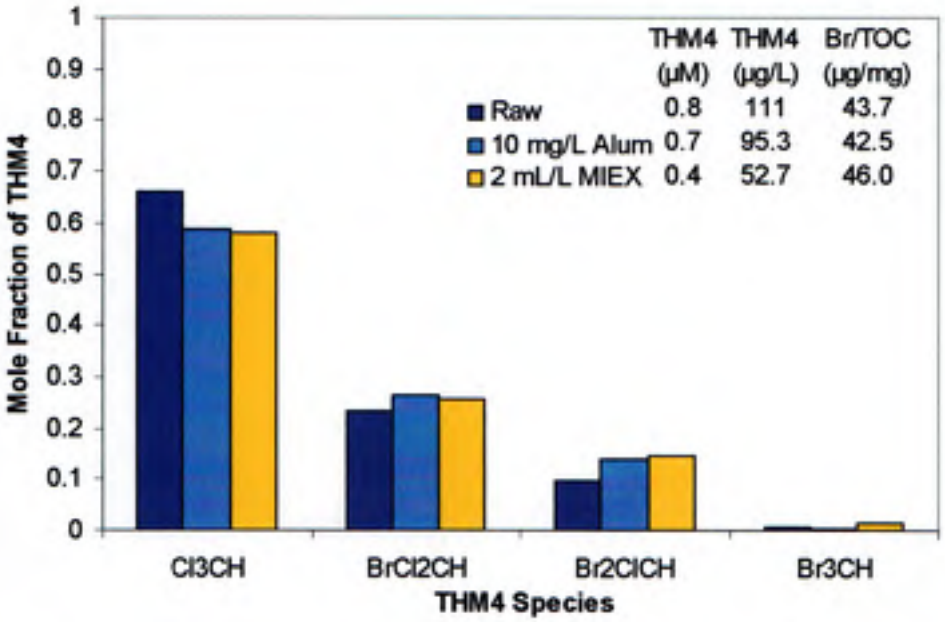

Figure D.1 Impact of coagulation and treatment with MIEX on THM speciation for SBA water

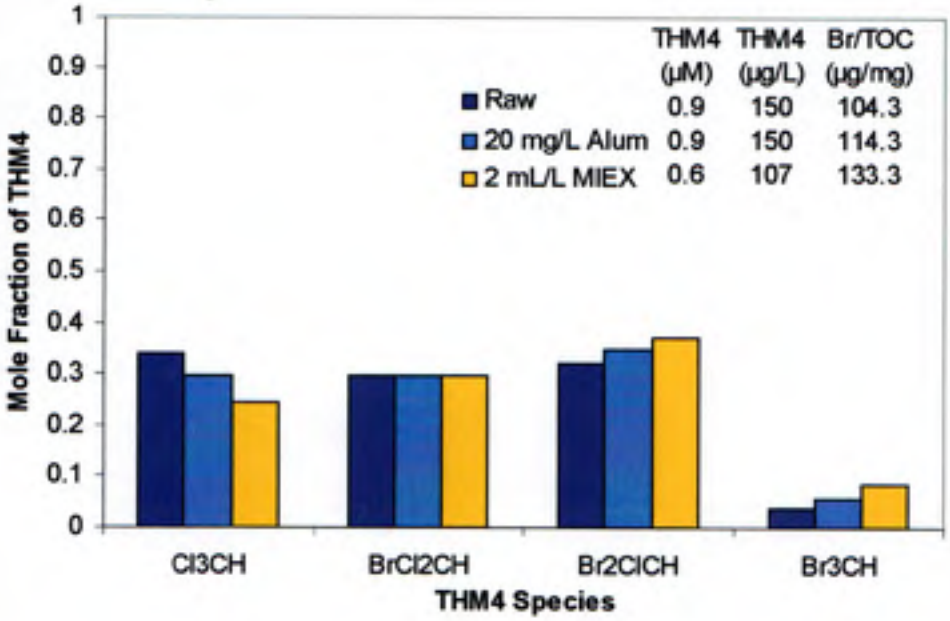

Figure D.2 Impact of coagulation and treatment with MIEX on THM speciation for CL water

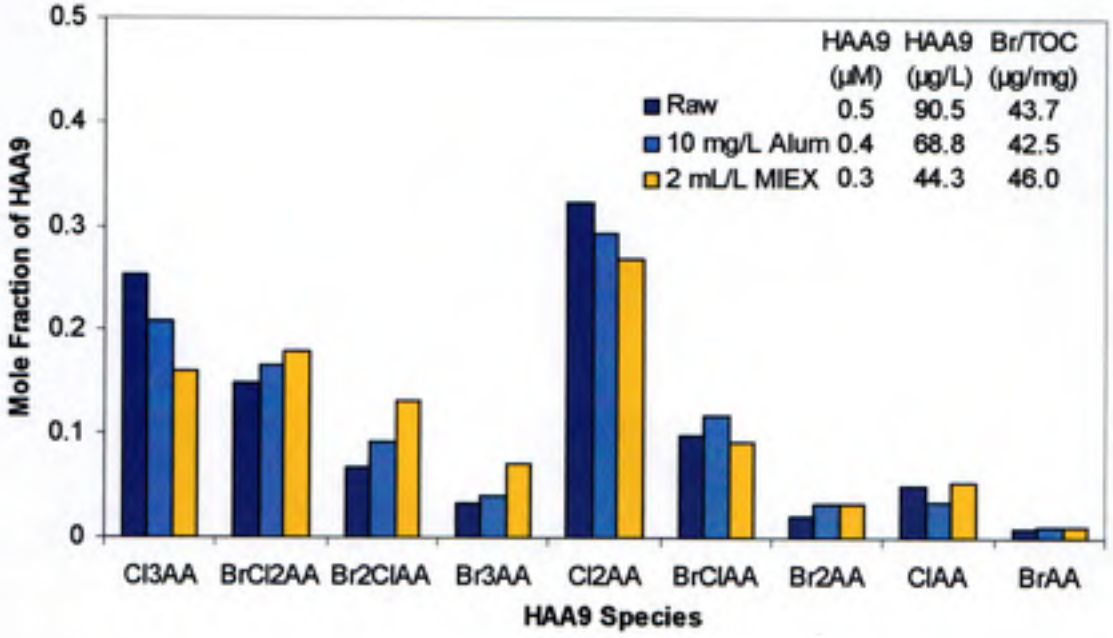

Figure D.3 Impact of coagulation and treatment with MIEX on HAA speciation for SBA water

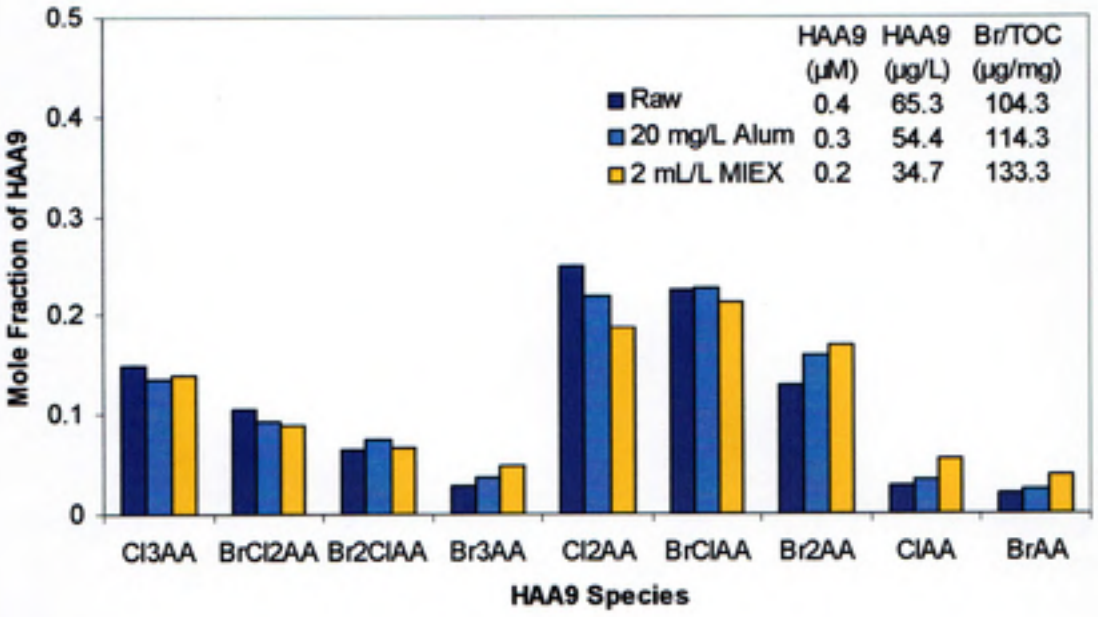

Figure D.4 Impact of coagulation and treatment with MIEX on HAA speciation for CL water

Appendix E
XAD Fractionation Results for CL and SBA Waters

This appendix contains the results of XAD fractionation experiments for CL water and SBA water. Fractions flagged with an asterisk (*) or dagger (†) indicate that the DOC concentrations are less certain (see § 4.5). Figure E.1 and Figure E.2 show the DOC concentrations for each XAD fraction for CL water and SBA water, respectively. Figure E.3 and Figure E.4 illustrate the impact of coagulation and treatment with MIEX on the removal of organic acid fractions for CL water and SBA water, respectively.

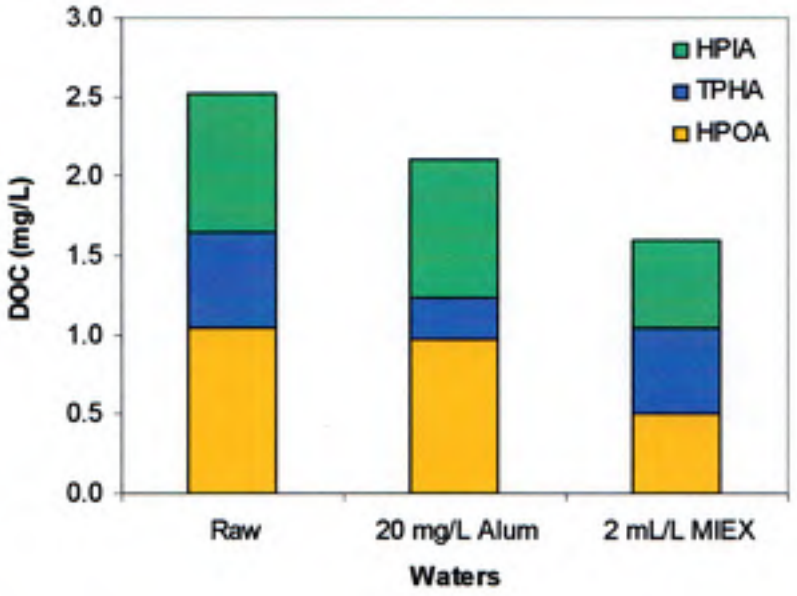

Figure E.1 Distribution of XAD fractions for raw and treated CL water (raw water SUVA 3.0 L $mg^{-1}m^{-1}$)

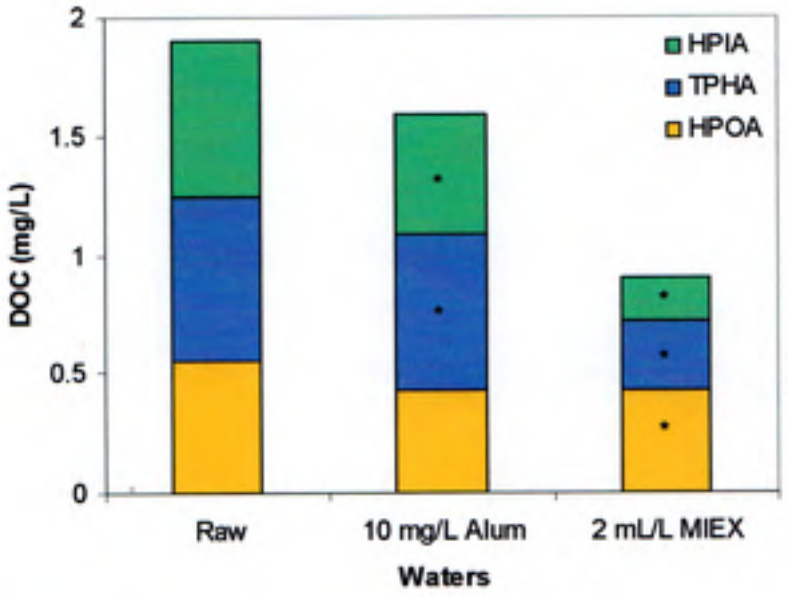

Figure E.2 Distribution of XAD fractions for raw and treated SBA water (raw water SUVA 3.4 L $mg^{-1}m^{-1}$) (* uncertain; see text)

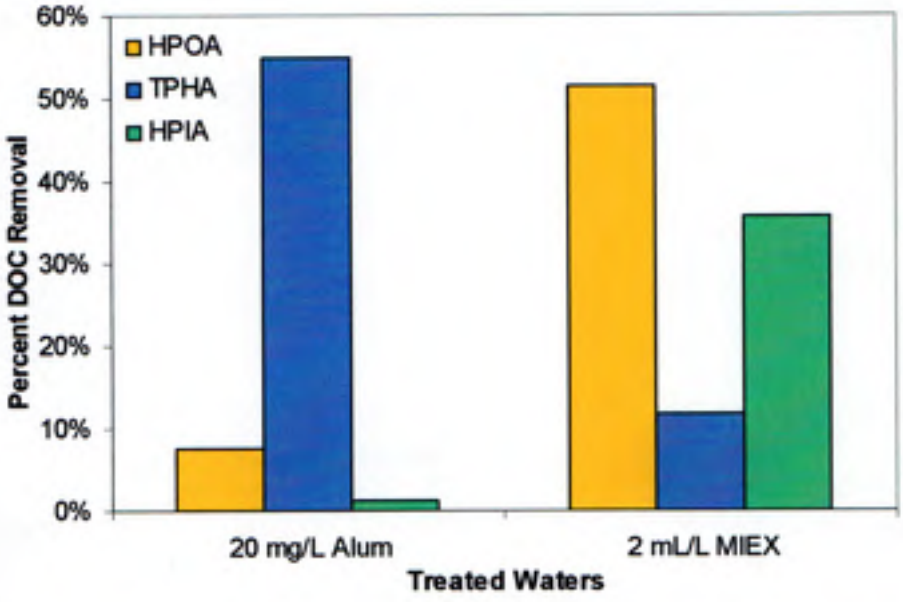

Figure E.3 Impact of coagulation and treatment with MIEX on the removal of organic acid fractions for CL water (raw water SUVA 3.0 L $mg^{-1}m^{-1}$)

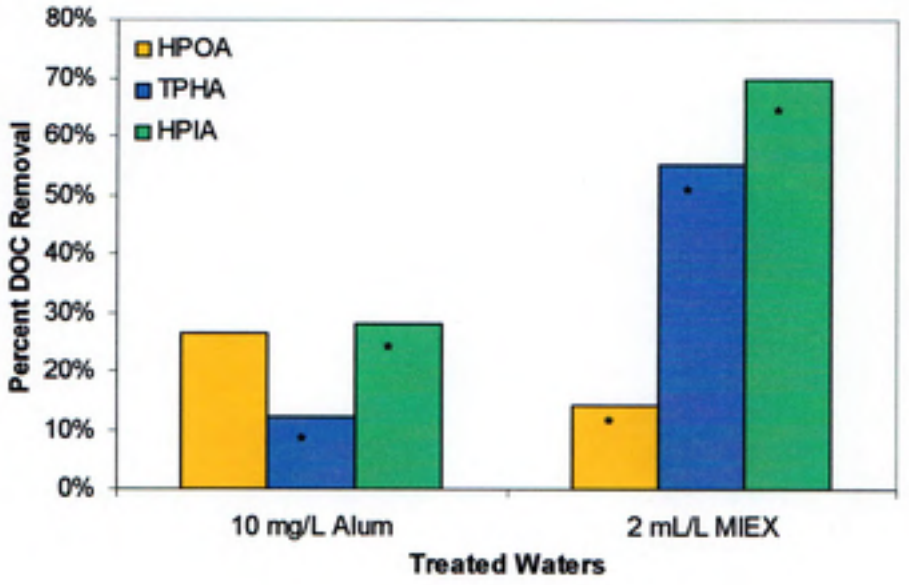

Figure E.4 Impact of coagulation and treatment with MIEX on the removal of organic acid fractions for SBA water (raw water SUVA 3.4 L $mg^{-1}m^{-1}$) (* uncertain; see text)

Appendix F
Molecular Weight Fractionation Results for CL and SBA Water

This appendix contains the results of molecular weight fractionation experiments for CL water and SBA water. Fractions flagged with an asterisk (*) or dagger (†) indicate that the DOC concentrations are less certain (see § 4.5). Figure F.1 and Figure F.2 show the DOC concentrations for each molecular weight fraction for CL water and SBA water, respectively. Figure F.3 and Figure F.4 illustrate the impact of coagulation and treatment with MIEX on the removal of molecular weight fractions for CL water and SBA water, respectively.

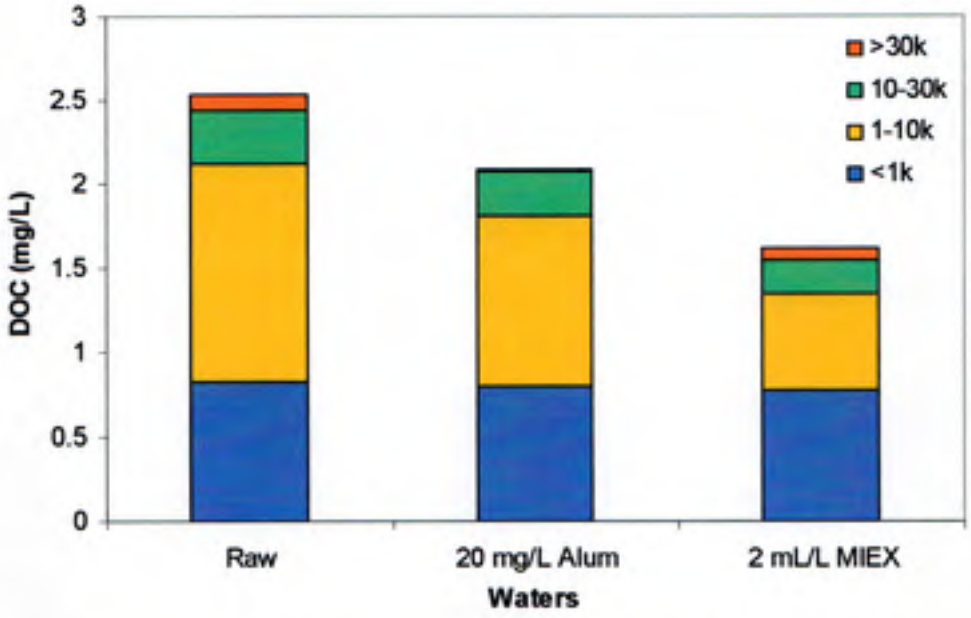

Figure F.1 Apparent molecular weight fractions of CL water before and after treatment (raw water SUVA 3.0 L $mg^{-1}m^{-1}$)

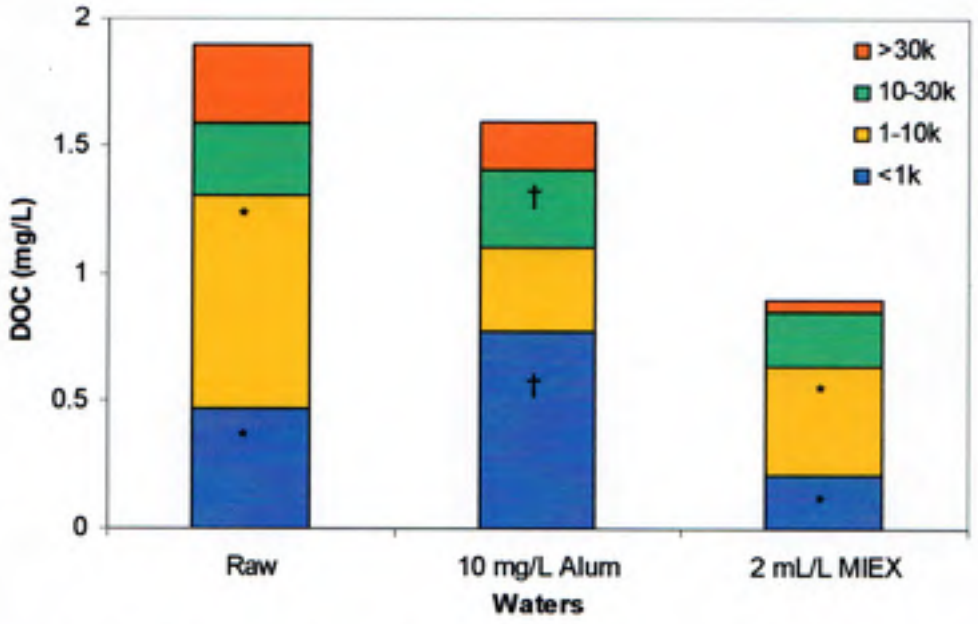

Figure F.2 Apparent molecular weight fractions of SBA water before and after treatment (raw water SUVA 3.4 L $mg^{-1}m^{-1}$) (*, † uncertain; see text)

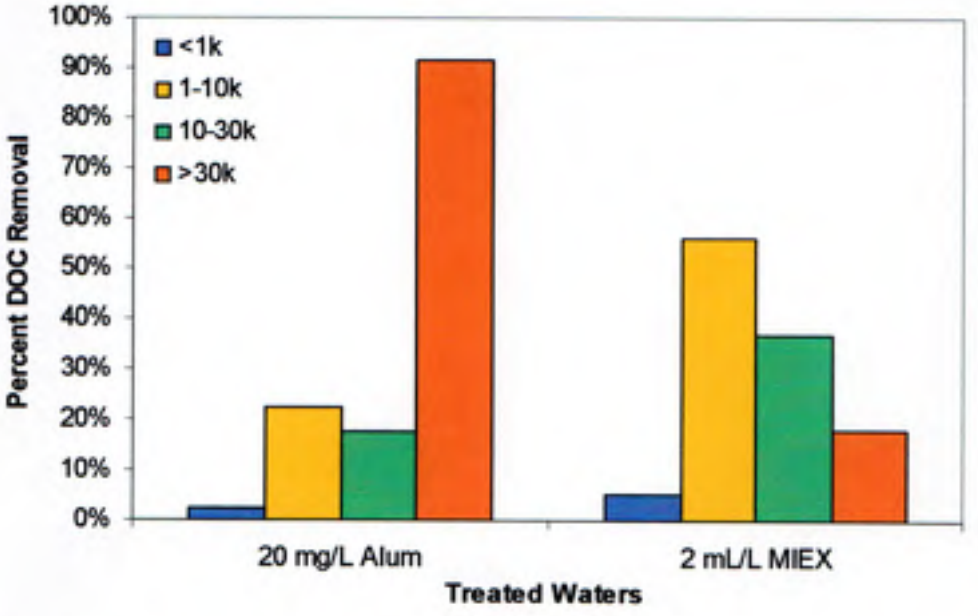

Figure F.3 Impact of coagulation and treatment with MIEX on the removal of different molecular weight fractions for CL water

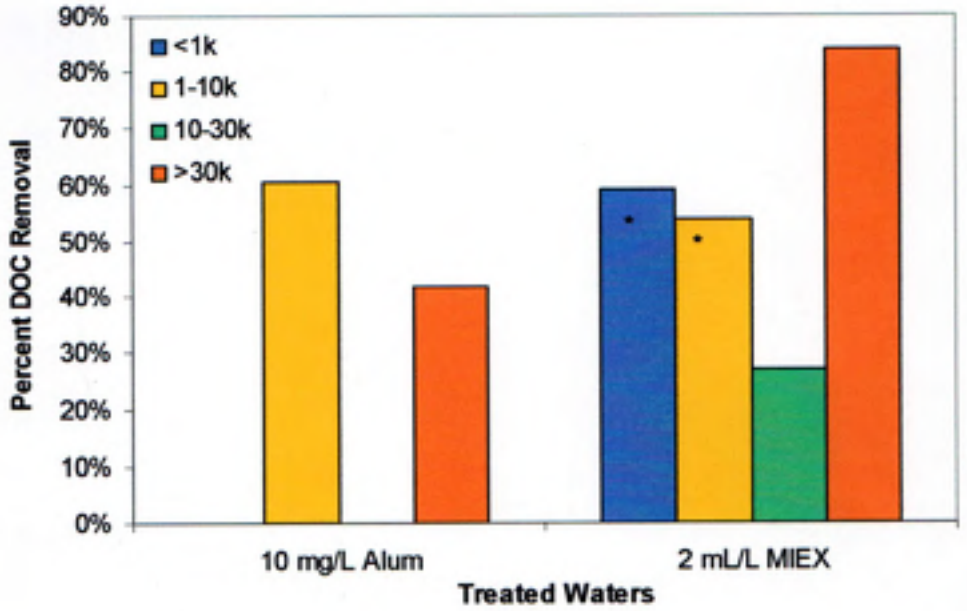

Figure F.4 Impact of coagulation and treatment with MIEX on the removal of different molecular weight fractions for SBA water (* uncertain; see text)

Appendix G
Linear Freundlich Isotherm for SL Water

This appendix contains the linearized Freundlich isotherms for MIEX, M-T, A641, and SIR based on DOC for SL water.

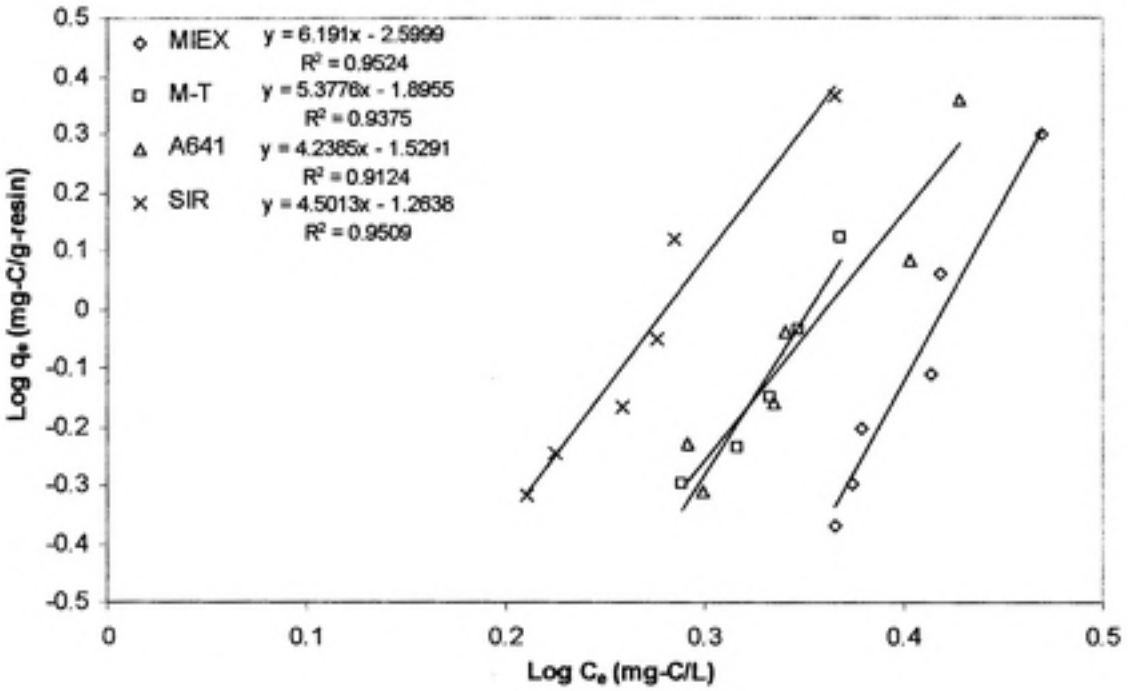

Figure G.1 Linearized Freundlich isotherms based on DOC removal for SL water

Appendix H
Ion Exchange Kinetic Results for SL Water

This appendix contains additional results from the kinetic study for SL water. Figure H.1 and Figure H.2 show the rate of UV absorbance removal and DOC removal, respectively, at a resin dose of 4 mL/L for MIEX, M-T, A641, and SIR.

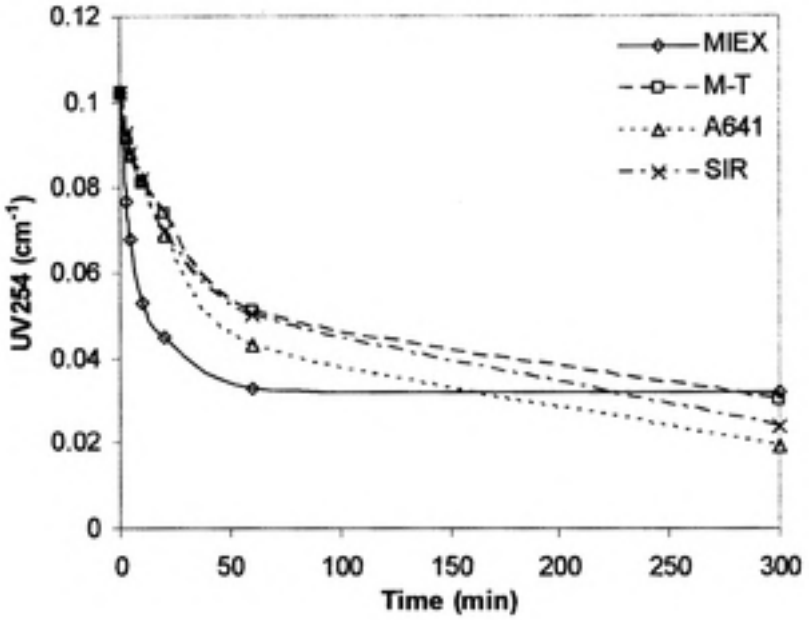

Figure H.1 Rate of removal of UV-absorbing substances by ion exchange treatment for SL water (4 mL/L resin)

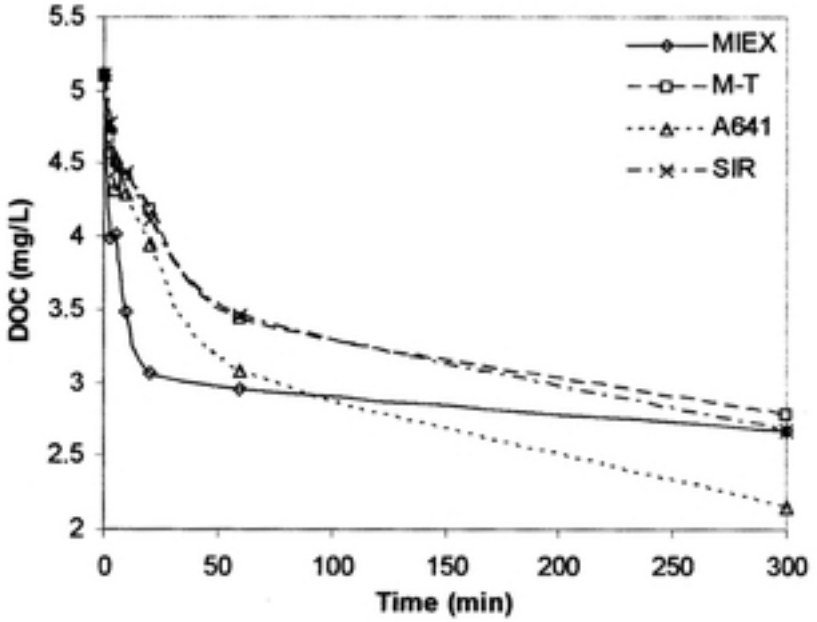

Figure H.2 Rate of DOC removal by ion exchange treatment for SL water (4 mL/L)